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**EUROPEAN PATENT APPLICATION**

21 Application number: 86307259.1

71 Int. Cl.<sup>4</sup>: **B 01 D 13/04**

**C 08 F 2/48, C 08 J 9/28**

22 Date of filing: 22.09.86

23 Priority: 23.09.85 US 778969 23.09.85 US 778970

24 Date of publication of application:  
01.04.87 Bulletin 87/14

25 Designated Contracting States:  
AT BE CH DE FR GB IT LI LU NL SE

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64 Microporous membrane laminate.

67 A membrane or laminate (10) consisting essentially of microporous polymerized material (12) consisting essentially of a precursor material which forms a homogenous solution with a liquid vehicle and is 1) rapidly polymerizable under ultraviolet or electron beam irradiation to a polymerized material, which is insoluble and nondispersible in the liquid vehicle, and 2) selected from the group consisting of organic monomers, organic oligomers, and mixtures thereof which are soluble in the liquid vehicle, the liquid vehicle being inert relative to the precursor material and optionally a support material (14) laminated directly to the microporous material. The precursor microporous material may include a hydrophobic monomer. The instant invention further provides a method for manufacturing the fluid permeable microporous membrane laminate (10) including the steps of mixing the precursor material into the liquid vehicle, forming the composition into a thin liquid layer, applying a support material (14) in intimate contact with the liquid layer, exposing the combined liquid layer and support material (14) to ultraviolet or electron beam irradiation to finally cure the liquid layer and form a laminate with the support material 14, and removing the liquid vehicle from the laminate (10).

## Description

## MICROPOROUS MEMBRANE LAMINATE

## TECHNICAL FIELD

5 The subject invention relates to a microporous organic polymeric membrane and the method for manufacturing the same. By "microporous membrane" it is meant a fluid permeable sheet or film having pores with a pore size of from 0.02 to 15 microns and having a thickness of less than 0.1 inches.

## BACKGROUND ART

10 Microporous membranes have great utility both as filtration media and as permselective barriers which retain particles or liquids while allowing the passage of gases and vapors. As barriers to bacteria, they are well known for their use in sterile filtration of liquids and gases in the medical, pharmaceutical and electronics industry. In other applications, the microporous membrane is utilized as a sterile hydrophobic vent, allowing the passage of vapor but preventing the passage of an aqueous solution.

15 There exists a number of additional areas in which the introduction of a microporous barrier would be useful but as to this date, no practical article exists. Modern medical techniques to reduce infection introduced in the operating room have more recently come to rely upon the use of operating room garments and surgical drapes fabricated from disposable nonwoven fabrics whose fibers have been made hydrophobic. These materials are in effect depth type filters, whose open spaces are far larger than bacteria, but whose density is such that the  
20 bacteria has a high probability of encountering and sticking to such a fiber. Even the best of such fibers do not retain more than 92 to 95% of the airborne bacteria. The use of "dense" coated fabric, on the other hand, is not possible because the garment or drape must breathe; that is, allow transport of air and water vapor in order to avoid hyperthermia in the patient and provide comfort to the operating theater staff. The use of a microporous membrane (hydrophobic or hydrophilic) with a pore size appropriate to act as a bacterial barrier clearly  
25 suggests itself to such an application.

Other applications, which require both the breathable aspect and the hydrophobicity, include disposable sheets to protect bedding, breathable diaper exteriors and other like applications. Microporous membranes have not been commercially applied to these uses for reasons of cost associated with slow rates of  
30 production, and because they have not usually had the correct combination of barrier properties and mechanical flexibility and softness. Moreover, most such polymer films are mechanically flimsy and their practical use is only extended by bonding them to microporous fabrics or paper supports, thereby forming a laminate structure.

Methods exist for the preparation of such fabric or paper supported laminates. Where the microporous  
35 membrane can be formed as a free, stand alone film element, the laminate may be formed by direct dot gluing, heat embossing or the provision of an intermediary layer which is melted to join the layers by locking into the pores of both materials. All of these techniques have the disadvantage of "blinding" surface pores and reducing flow efficiency. Alternatively, under some circumstances the microporous membrane may be formed directly on the support material. A laminate of this type can only be formed provided that the polymer solution, from which the membrane is created, is of sufficient viscosity. Furthermore, the support material must be of  
40 sufficient density and not impaired either by the solvent system or the aqueous washing baths and drying ovens used in the process.

The U.S. patent 4,466,931 assigned to the assignee of the instant invention discloses a method whereby a microporous membrane is prepared by the exposure of ultraviolet radiation or electron beam radiation of a  
45 solution of acrylic oligomers and/or monomers in a solvent or mixture of solvents which is a nonsolvent for the polymer formed as a result of the exposure. The class of monomers and oligomers most noted for this characteristic of undergoing rapid polymerization under electron beam or ultraviolet radiation are: the polymerizable unsaturated organic compounds having a double bond between two carbon atoms, at least one of which has also bonded thereto a carboxyl, carboxylate ester or amino functionality; the epoxies and other cyclic ethers; and thioleues.

50 When ultraviolet radiation of sufficient intensity in the 200 to 400 nm range is present, and in the presence of photoinitiator molecules which capture ultraviolet light and promote the polymerization reaction, or by the rapid injection of electrons from an electron beam, the process of polymerization and simultaneous phase separation can be made to take place with great rapidity and production speeds greater than 100 feet per minute can be achieved. With an appropriate electron beam, line speeds in excess of 300 feet per minute are  
55 possible. The crosslinked microporous film produced by either technique must still be washed free of the original solvent, which remains in the pores after polymerization, and subsequently dried.

Due to the very high rate of manufacture compared to conventionally prepared microporous membranes, there is great advantage to the preparation of ultraviolet or electron beam polymerized membrane as a laminated layer bonded to a fabric or paper support material. However, due to the low viscosity of the solutions  
60 normally used (10 to 50 cps), it is very difficult to utilize conventional methods of surface coating. Such techniques will not support thin liquid layer unless the support material is quite dense.

Additional problems are presented with support materials which do not have a homogenous superstructure. Defects or openings in the superstructure are non-uniform. Unless the support is extremely dense, such

supports are difficult to coat without the formation of defects, such as holes, in the coated layer. In addition, the line speed must be sufficiently fast such that the residence time of the coating solution on the support, until completion of the polymerization, is shorter than the time for it (the solution) to wick into the support matrix.

Another problem relates to the preparation of hydrophobic membranes from ultraviolet or electron beam curable materials. In the aforementioned United States Patent 4,466,931, all of the oligomers tested yielded intrinsically hydrophilic membranes. Moreover, conventional post-preparation treatments to render the membrane hydrophobic, such as dipping the membrane in solutions containing silicone or perfluorocarbon additives do not yield satisfactory results. Neither did the addition of vinyl terminated silicones or long chain hydrocarbon acrylate esters to the coating solution. Additional problems include identification of the specific chemical structure of an oligomer appropriate to utilize for several of the applications of interest, which require flexibility and toughness. At the same time the material must also have sufficient mechanical strength so that the forces due to the large internal surface area do not cause the collapse of the porous structure. This concern must also be true of the washing solvent which is used to wash out the curing solvent; that is, it must not attack or soften the microporous structure and cause the film to collapse.

The instant invention provides a basis for the preparation of a hydrophobic microporous membrane laminate which, at its optimum, possesses a microporous membrane coating that is flexible and rubbery in character, and yet has superior strength characteristics and resists collapse of the superstructure.

#### STATEMENT OF THE INVENTION

According to the present invention there is provided a method for manufacturing microporous membranes (10) comprising the steps of:

A. mixing into a liquid vehicle a precursor material which is 1) rapidly polymerizable under ultraviolet or electron beam irradiation to a solid polymer, which is insoluble and nondispersible in the liquid vehicle such that when the polymers are formed it rapidly segregates from the liquid vehicle, and 2) selected from the group consisting of the organic monomers, the organic oligomers and mixtures thereof which are soluble in the liquid vehicle whereby upon said mixing there results a composition which is a liquid solution of said material in said liquid vehicle, said liquid vehicle being chemically inert relative to said material;

B. forming said composition into a thin liquid layer;

C. exposing the liquid layer to ultraviolet or electron beam irradiation to finally cure the liquid layer and to form a laminate with the support material (14), and

D. removing the liquid vehicle from the membrane, characterized in that the precursor material includes a hydrophobic monomer or monomers and/or a support material is applied into intimate contact with the liquid layer before final curing thereof.

The invention also provides a membrane comprising a microporous polymerized layer (12) of a precursor material which forms a homogenous solution with a liquid vehicle and 1) is rapidly polymerizable under ultraviolet or electron beam irradiation to said polymerized material (12), which is insoluble and nondispersible in the liquid vehicle, and 2) is selected from the group consisting of the organic monomers, the organic oligomers and mixtures thereof which are soluble in the liquid vehicle, the liquid vehicle being inert relative to said precursor material, characterized in that said precursor material includes a hydrophobic monomer or monomers and/or a support material (14) laminated directly to said microporous polymerized material (12).

Preferably the precursor material includes a hydrophobic monomer or monomers which, as hereinafter more fully described, imparts hydrophobic properties to the membrane.

The membrane may be formed as a laminate by applying a support material into intimate contact with the liquid layer before final polymerisation thereof; however the membrane may also be formed without so-laminating, for example on a release-coated carrier sheet from which it may be removed after polymerisation.

#### FIGURES IN THE DRAWINGS

Other advantages of the present invention will be readily appreciated as the same becomes better understood by reference to the following detailed description in connection with accompanying drawings wherein:

Figure 1 is a cross sectional view of a membrane constructed in accordance with instant invention;

Figure 2 is schematic depiction illustrating the subject method;

Figure 3 is a schematic depiction of the subject method;

Figure 4 is a schematic depiction of an alternate method for making the embodiment shown in Figure 5;

Figure 5 is a cross sectional view of a second embodiment of the instant invention; and

Figure 6 is a chart illustrating the effect of precure dose on air flow;

Figure 7 is a micrograph showing the top surface of a film as made in example 11;

Figure 8 is a micrograph showing a cross section of the film as made in example 11;

Figure 9 is a micrograph of the top surface of a film as made in example 12; and

Figure 10 as a micrograph showing a cross section of the film as made in example 12.

## DETAILED DESCRIPTION OF THE DRAWINGS

A membrane laminate constructed in accordance with the instant as generally shown at 10 in Figure 1. The membrane laminate 10 consists essentially of a microporous polymerized material 12 and a support material 14 laminated directly to the microporous material 12.

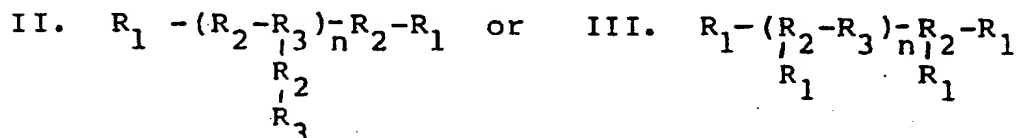
The microporous polymerized material 12 consists essentially of a precursor material which forms a homogenous solution with a liquid vehicle and (1) is rapidly polymerizable under ultraviolet or electron beam irradiation to the polymerized material 12, which is insoluble and nondispersible in the liquid vehicle, and (2) is selected from the group consisting of the organic monomers, the organic oligomers, and mixtures thereof which are soluble in the liquid vehicle. The liquid vehicle is chemically inert relative to the precursor material, and a nonsolvent for the polymerized material.

The oligomeric materials which have been found specifically suitable for the subject invention and the intended applications thereof are acrylic polyester urethanes of the general Formula I:



where  $R_1$  is the radical of an hydroxyterminated acrylate monomer such as hydroxyethylacrylate, hydroxypropylacrylate and 4-hydroxybutylacrylate.  $R_2$  is the dicarbamate or tricarbamate group resulting from the reaction of the isocyanate materials selected from the group consisting of di- and tri-aliphatic or aromatic isocyanates such as toluenediisocyanate, hydrogenated methylenedianiline diisocyanate, trimethylhexane diisocyanate, methylenedianiline diisocyanate and isophoronediiisocyanate.  $R_3$  is selected from the group of polyester polyols made of the condensation of adipic acid with each one or of a mixture of ethylene glycol, diethyleneglycol, butanediol, hexanediol and neopentylglycol and which may also contain isophthalic acid and phthalic acid residues to increase rigidity or some triols such as trimethylolpropane or glycerine to introduce higher functionality. It can also be made of polycaprolactone diol or triols, and  $R_3$  can have a number average molecular weight of 200 to 3000 and  $n$  may range from 0 to 4.

The above general Formula I describes the situation with difunctional isocyanate and difunctional polyol precursors. It can be modified to Formulas II and III in order to describe the structure of the polyfunctional acrylates which result from using trifunctional polyol and trifunctional isocyanates respectively: that is,



The above described family of oligomer members have been found suitable to span the requirements for either rigid filtration materials or to provide a laminate which is uniquely flexible and provides a rubbery character while being sufficiently strong to provide the properties consistent with the intended nonfiltration, microbial barrier or liquid barrier applications of the subject article.

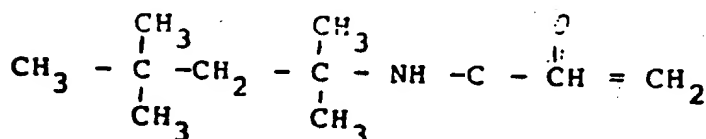
The oligomeric formulation is preferably in a combination such that the weight percent nitrogen obtained from elemental analysis, and associated with the carbamate functionality, as measured by the Dumas technique is in the range of  $1.5 \pm 0.3\%$  to  $6.2 \pm 0.3\%$ . It should be noted that for oligomers in the range between 1.5 - 4% nitrogen (associated with the isocyanate functionality) the presence of crosslinking agents and/or comonomers will usually be necessary in order to obtain a microporous film.

It is not necessary that the oligomer of the membrane layer 12 be a single oligomer of the above type, but may constitute a mixture or blend of two or more oligomers. In this event, the lower, preferable limit of the average percent nitrogen as carbamate in the mixture or blend will depend on the percent nitrogen (as carbamate) of the component of lower value. For example, a blend of a resin with a percent nitrogen of 1.5% combined with a second resin of 6% may require an average percent nitrogen (on the mixture) of 2.3%, whereas a blend with a resin of 1.7% nitrogen may only require a minimum average (on the mixture) of 2%.

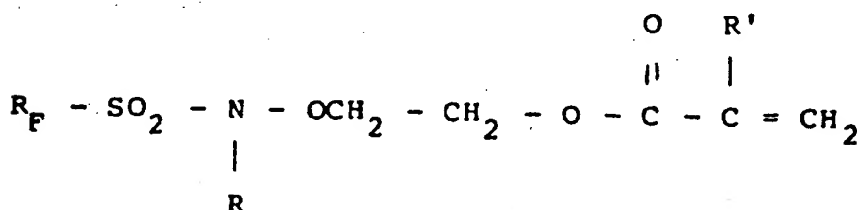
In addition to acrylic polyester urethane oligomer, it is often useful and sometimes necessary to add a crosslinking monomer with the oligomeric precursor material and the liquid vehicle. The cross linking monomer may be chosen from the group of difunctional and trifunctional cross linking monomers for the purpose of adding strength and stabilizing the membrane against collapse. The examples of such materials are 1,4-butanedioldiacrylate (BDDA), 1,6-hexanedioldiacrylate (HDDA), trimethylolpropanetriacrylate (TMPTA), tetraethylene glycol diacrylate (TEGDA), and tripropylene glycol diacrylate (TPGDA), neopentyl glycol diacrylate, polyethylene glycol diacrylates, polypropylene glycol diacrylates, 1,3 butylene glycol diacrylate and the diacrylates and triacrylates derived from ethoxylated and propoxylated diols and triols which are mentioned in the above di and triacrylates. The membrane 12 may include these materials in order to provide specific desired combinations of mechanical properties, pore size, and void volume. Experimentation has shown that these materials should not constitute more than 50% (wt/wt) of the polymerizable material in the system. In addition to polyfunctional acrylates, monomers such as acrylic acid, N-vinylpyrrolidone, N-vinylcaprolactam, 2-ethylhexylacrylate, phenoxyethylacrylate, isobornylacrylate, dicyclopentadienyl ethyl acrylate, tetrahydrofurfuryl acrylate, ethyldiglycolacrylate, hydroxyethylacrylate, hydroxypropylacrylate, butylcarbameylethylacrylate and isobutoxymethylacrylamide, can also be added either by themselves or with the crosslinking monomers such that the total content of monomers is in the range of up to 50% of the polymerizable solids content. The

function of the monomers is to increase flexibility, modify mechanical properties or to introduce a desired chemical groups such as carboxylic or hydroxy groups.

The microporous films previously produced from the combination of oligomer and crosslinking monomer are near hydrophilic and intrinsically wettable with water. A hydrophobic membrane laminate may be produced by the addition of a hydrophobic monomer to the microporous material. The addition of either of the monomers 1,1,3,3-tetramethylbutylacrylamide having the formula

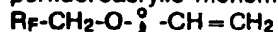


(t-octylacrylamide or TOCTAM) and/or perfluoromonomer of the general structure



where  $\text{R}_F$  is the perfluoroalkyl radical,  $\text{C}_k\text{F}_{2k+1}$ , where  $k$  is essentially 6 to 10,  $\text{R}$  is of the formula  $\text{C}_m\text{H}_{2m+1}$

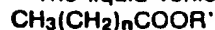
where  $m = 2-4$ , and  $\text{R}'$  is hydrogen or methyl, providing hydrophobicity to the microporous film, or a perfluoroacrylic monomer of the structure



where  $\text{R}_F = \text{C}_z\text{F}_{2z+1}$ , and  $z = 6-8$ . When utilizing TOCTAM, the hydrophobic monomer would comprise preferably no less than 80% and no more than 30% by weight of the polymerizable material in the formulation. The perfluoromonomers should be present as no less than 30% and no more than 25% (weight/weight) of the total polymerizable components of the solution. This relatively small amount of monomer provides hydrophobic characteristics to the laminate. Alternatively, independent membrane, not laminated to a support, may be manufactured also including the excellent hydrophobic characteristics. That is, membrane made from the precursor material of the instant invention, but not laminated to a support material, may be made hydrophobic pursuant to the addition of the aforementioned monomers.

It is believed that the hydrophobic monomer segregates upon polymerization to provide a continuous hydrophobic surface at the interface between the polymerizing material and the remaining solution. The aforementioned results are unexpected for several reasons. Firstly, the hydrophilic nature of the membranes without the monomer is a query because of the relatively hydrophobic character of the organic compounds comprising the monomers or oligomers used as precursors. However, it has been found that such membranes are nonetheless intrinsically wettable. Secondly, the addition of the small amount of monomer to the precursor solution forms a homogenous one phase solution. From this homogenous solution, the hydrophobic monomer somehow segregates itself during polymerization to cause the formation of a hydrophobic surface which possesses hydrophobic barrier properties. Finally, it is unexpected that the hydrophobic monomers behave as hydrophobic agents despite their originating in relatively low concentration in a homogenous solution, as opposed to hydrophobic agents such as dimethyl siloxanes or stearyl compounds which are surface deposited in a post-treatment or the specific grafting of the hydrophobic fluoromonomer to the hydrophilic structure in a separate post polymerization treatment. The latter treatments are described in detail in the paper of Heckman and Strickler in Vol. 5 of the Index 84 Congress organized by the European Disposables and Nonwovens Association. With respect to the behavior of the t-octylacrylamide, it seems that the hydrophobic character imparted is related to the compact stereochemical structure of the methyl groups in the t-octyl radical, since lauryl acrylate, which contains a linear hydrocarbon chain with a larger number of carbon atoms (12), does not show the effect. The effect of TOCTAM is unexpected since normally linear paraffinic chains exhibit better hydrophobicity than branched ones and the water repellency characteristic is normally achieved with longer than 8 carbon atoms in the chain. C14 to C20 straight hydrocarbon chains are usually used. The instant invention provides a hydrophobic material and does not require a post treatment. Further, the instant invention provides a hydrophobic microporous membrane which is not contaminated or obstructed by an additional silicon or other surface agent.

The liquid vehicle or solvent is preferably chosen from the group having the formula



where  $\text{R}'$  equals methyl, ethyl, isopropyl, and  $n$  equals 6-16 or,



where n equals 3 to 8 and R\* equals methyl, ethyl, isopropyl, butyl, isobutyl, octyl and isooctyl. For example, the group consists of methyl, ethyl or isopropyl esters of capric, caprylic, caproic, lauric, myristic and palmitic acids (namely: linear fatty acids of 6-16 carbon atoms), dimethyl, diethyl, diisopropyl, diisobutyl, diisooctyl, dibutyl and dioctyl esters of glutaric, adipic, azelaic and sebacic acids. These esters can be used alone or as mixtures with one another of the above group of esters as well as in combinations with the butyl ether of ethylene glycol acetate, also known as butyl cellosolve acetate, because of their specific solubility compatibility properties toward the oligomers and monomers, and their general characteristics of having a very low toxicity, volatility and flammability. Depending on the pore size and void volume required for the particular membrane application, the weight percent of total solvent in the solution to be polymerized may range from 40 to 80%. Reducing the weight percent of solvent in the solution, i.e. increasing the weight percent of polymerizable solids, tends to reduce the pore size. Depending on the mechanical strength of the polymerized material, this can sometimes lead to collapse of the microporous matrix due to the very large force generated by the large internal surface area multiplied by the interfacial energy. In such cases a transparent or partially opaque membrane will result.

It has further been determined that the temperature at which the initially transparent solution of the oligomer and monomers first becomes hazy to the eye (the cloud point) is strongly correlated to the largest pore size of the microporous film which results. As the cloud point temperature drops, the pore size becomes smaller. Such behavior is indicative of the fact that the solvent or solvent mixture chosen is a better solvent for the oligomer and not as bad a nonsolvent for the resultant polymer. To obtain membranes with pore sizes in the 0.05 to 0.5 micrometer range, solutions containing 35% polymerizable solids and possessing cloud points between 10°C and 40°C are optimal for several of the oligomer systems examined.

The cloud point not only serves as a guide with respect to the pore size to be anticipated in the final microporous membrane, it also serves as a valuable guide with respect to the operating temperature at which the process should be carried out. Since the cloud point represents the first instability and onset of phase separation in the precursor solution, it is preferable to carry out the process at a temperature of at least 2 degrees above the observed cloud point. The major reason for this is that the system is most reproducible under these conditions. However, this does not mean that the process cannot be operated at temperatures near or even below the cloud point of the solution. Under such conditions it must be kept in mind that some liquid-liquid phase separation may occur and that this will change the distribution of the pore size and the structure of the resultant membrane. Since such situations are by their nature time dependent and difficult to control, it has been found to be advisable to work in the stable, single phase situation which is to be found at least 2 degrees above the cloud point. However, since this temperature depends on specific chemical interactions between the solvent (including any photo initiator and surfactant present) and oligomer, this temperature range is only an approximate guide and cannot be generalized.

While most solutions which are in the homogenous, stable region are optically clear, it has sometimes been found that due to the presence of a small quantity of a high molecular weight fraction of an oligomer, an apparently stable solution demonstrates a certain amount of cloudiness or haze. The presence of such a haze does interfere with the determination of the cloud point and for this reason such systems are not preferable. However, the presence of this fraction, as indicated by the haze, does not appear to affect the properties of the final membrane, as we have examined solutions which have been clarified either by filtration or centrifugation from this fraction and the properties of the final membranes produced in either case from the same solution have been almost identical.

Surfactants may be mixed with the oligomer in the liquid vehicle. Surfactants, such as DC-193, a copolymer of polydimethylsiloxane and a polyether (Dow Corning Corp.) may be used to obtain sufficient spreading of the solution on an appropriate paper or moving belt. Surfactants, as well as photoinitiators used for ultraviolet cured materials, may change the cloud point and influence adhesion of the polymerized membrane 12 to a specific support substrate.

Unexpectedly, the instant invention can provide a laminate having strengthened superstructure properties wherein the porosity and transfer characteristics of the laminate are actually better than the free film. The instant invention provides a microporous membrane-support layer laminate without gluing wherein adherence of the membrane 12 to the support material 14 increases mechanical stability.

The support material 14 may be a woven or nonwoven fabric. Excellent adhesion of the microporous membrane 12 to the support material 14 may be achieved by the support material consisting essentially of a polyamide or polyester nonwoven fabric in the range of 0.3 ounces per square yard to 1.5 ounces per square yard. Excellent results have also been obtained where the support material 14 is a polypropylene nonwoven fabric which is corona discharge treated at a minimum of 6.5 watt-minutes per foot and used within less than 24 hours, with electron beam irradiated material. Optimum results are obtained for both UV and EB curing by in-line corona discharge.

A nonwoven cellulosic derivative may also be used. For example, the microporous membrane 12 may be laminated to a common paper material.

The instant invention provides a method for manufacturing the fluid permeable microporous membrane 10. The method essentially includes the steps of mixing into the liquid vehicle the precursor material, forming the composition into a thin liquid layer, applying a support material into intimate contact with the liquid layer, exposing the combination of the liquid layer and support to ultraviolet or electron beam irradiation to finally

cure the liquid layer and to form a laminate with the support material. These steps of the method, with the exception of the final wash step, are illustrated in Figures 2-4. The step of removing the inert solvent from the roll of laminate at roller 32 in Figure 2 may be accomplished by the use of any appropriate fabric washing apparatus consisting of baths and/or sprays which does not mechanically crush the microporous structure of the coating. An example of such an apparatus is the Permasol F machine (Jawetex Company, Switzerland).

As shown in Figures 2-4, the thin liquid layer may be exposed to electron beam or ultraviolet radiation to partially polymerize the material prior to application of the support material. This step takes place in the presence of atmospheric oxygen. This causes the partial polymerization of the liquid layer and brings it to a point that it does not easily flow. The optimum extent of polymerization must be determined experimentally for a given composition and web speed; the web speed being the speed of the support on which the liquid is layered. The polymerization level is dictated in part by the electron beam dose rate or the strength of the UV lamps. Since UV lamps are not infinitely variable in their output, like electron beam equipment, various filter arrangements may be necessary to control the cure dose rate. The most serious result of over cure is a lack of lamination adhesion while that of under cure is the presence of pinhole defects in the membrane.

Example 3 and Figure 6 illustrates the effect of precure doses on air flow properties. The effect was also shown in Figure 6 as the dependency of the air flow of the membrane on the relative conversion of the crosslinking monomer after the stage of precure and prior to the lamination stage. The data for percent conversion of the monomer serves to indicate the relative degree of polymerization. It was determined by analyzing residual nonpolymerized monomer after the stage. The different levels of conversion have been achieved by attenuation of the precure dose and relate to the same set of air flow versus precure dose data points. Zero precure irradiation or zero crosslinking still provides a polymer/support combination having transport properties. Such a composite or mechanically reinforced material has maximum fiber reinforcement as the prepolymerized material wicks, or is absorbed into, the interstitial spaces of the support material 14 prior to final irradiation.

It has been determined that the presence of atmospheric oxygen is required in the partial cure step in order to obtain good adhesion in the following step in which the fabric substrate is laminated to the partially polymerized solution. As shown in Figure 2, the manufacturing system includes a continuous belt 16 driven from roller 18 to roller 20. The mixture of solvent and precursor material are applied to the belt at 22. It is at this point that the composition is formed into a thin liquid layer. The thin liquid layer of the composition is precured by exposure to ultraviolet or electron beam irradiation at 24. The support material 14 is brought into intimate contact with the liquid layer by roller 26, as shown in detail in Figure 3. The combination is then conveyed under one or more ultraviolet lamps or an electron beam curing head 28 to complete the polymerization of the microporous film 12. The microporous film 12 is now laminated to the fabric substrate.

The ultraviolet lamps for carrying out the polymerization may be accomplished through the fabric support 14 as shown in Figure 2. This is totally unexpected in view of the report of Gray III et al as recited in the U.S. patent 4,289,821 wherein it was stated that radiation by ultraviolet light can only penetrate optically clear substances. The curing by ultraviolet light may also be accomplished by irradiation through a moving belt if the material of the belt is made from an optically clear, silicone release treated, polypropylene or mylar film. Hence, it is possible to effect a final cure using ultraviolet light which is directed from above the support 14 or below the belt 16.

Once finally cured, as shown in Figure 2 it is still possible to either perform an additional coating with the same or a different composition coating solution and of the same or different thicknesses, or to wind up the cured laminate on roller 32. For example, the polymerized laminate 10 is removed from belt 16 over roller 35. A second material formulation of precursor material is applied to belt 16 at 36 and irradiated at 38, the laminate material 10 being added at point 40. The material 10 is then finally cured at station 42 and rolled onto rollers 32 as the belt 16 is rolled onto roller 20.

A second alternative is shown in Figure 4 wherein a first laminate 10 is formed from the left on support material 16 and a second laminate 10' is formed on support material 16' (like components being numbered and primed) and the two cured membrane surfaces are combined at lamination nip rolls 44 and irradiated at 30, as discussed above, to form a dual layer laminate having a support surface on the outer surface of each laminate. The membrane layers are adhered by the application of a layer of precursor material by kiss roller 45. The product formed is rolled onto roll 46 and illustrated in Figure 5. The ability to create multiple microporous layers which become chemically grafted to one another and which can have different physical chemical properties is one of the major advantages of the instant invention. It is very often the case that formulations which have the best mechanical properties lack adhesion or may also display an unwanted degree of adhesiveness towards a support, which is a phenomenon which is known in the textile industry as "blocking". Thus it is possible to coat an initial layer with one set of properties for adhesion, a middle layer which has the correct bulk mechanical properties which one desires in the coating and even complete this with a specialized top coating if necessary. An obvious by-product of this technique is also the fact that any macroimperfections in the coating are also covered up by one or another of the layers.

Although the cured laminate still contains the original solvent in its pores, the pore formation process is over the moment the cure is complete and the material has been found to be quite stable in this form. Thus, the still wet roll can be stored for washing at a later time. This feature of the subject invention is a significant advance over the prior art since it does not require the washing process and the curing process to either operate at the same line speed or have multiple roll arrangements which compensate for large differences in the line speed.



However, the wind up speed must be maintained so that the tension in the roll is controlled such that the microporous structure is not crushed by the tightness of the wrap. Since this parameter is a function of the specific oligomer and support fabric used, the tension limit must be determined for every given combination.

The washing process is performed in baths containing a solvent which efficiently removes the curing solvent remaining in the pores and which does not attack or soften the crosslinked polymeric film. This is because the internal surface area of the microporous film is very large and if the material has been softened to the point that the force resulting from the interfacial tension multiplied by the internal area is greater than its tensile strength, the microporous structure will undergo some degree of collapse. Examples of washing solvents are perchloroethylene, methylene chloride and 1,1,2-trifluorotrichloroethane (FREON 113, Dupont) and mixtures of low alcohols, acetones, and chlorinated solvents with FREON 113. For the family of acrylic urethane polyester oligomeric materials specifically well suited for the instant invention, FREON 113 has been found to be the most appropriate due to its insolubility in the polymerized polymer in the wash. Perchloroethylene or other chlorinated solvents together or alone may cause collapse of the porous structure. Moreover, the FREON 113 has a very low toxicity, is not flammable or explosive, and requires very low energy to remove it in the drying step. An additional advantage is that it has a high extraction coefficient towards residual monomer, oligomer and, in the case of ultraviolet curing, photoinitiator. Thus the resulting membrane material is sufficiently clean and free of potential contaminants whereby it is capable of passing the U.S.P. class VI testing of plastic materials for medical devices.

The laminates of the instant invention include properties, as illustrated in the following examples, which make the laminate an excellent substrate for use as breathable, sterile barriers. Such breathable, sterile barriers may be utilized for purposes associated with medical, disposable nonwoven fabrics as well as the outer covers as hydrophobic, breathable barriers, specifically as the external layer of a diaper or feminine hygiene product.

## EXAMPLES

### A. Definitions and Terms:

**Air flow:** expressed in ml/min at a pressure differential of 80cm height of water on a 5 square disc of the laminate.

**WWR:** Wire wound rod used to lay down the coating. The rod number times a factor of 1.9 gives the approximate wet thickness in microns.

**Washing and drying:** is the process of thorough washing of the porous product in 1,1,2-trifluorotrichloroethane, also known as FREON 113 or FREON, and subsequent drying at room temperature.

**Light dose or Radiation dose:** expresses the effective UV energy to which the coating is exposed. The numbers in joule/cm<sup>2</sup> are taken from the reading of the International Light Radiometer, Model IL745 with Light Bug A309, which has its maximum response at about 350nm.

**Energy flux or Radiation flux:** expresses the effective near UV energy output of one cm length of the lamp after said attenuation.

**Bubble Point (BP):** is the pressure of air required to displace, from the largest pores in the membrane, a liquid which wets the porous structure completely. In the following examples the BP test is done with kerosene as the liquid. The bubble point is inversely proportional to the pore size, and a Kerosene BP of 1 bar is approximately correlated with a pore size of 0.4 microns.

**Water breakthrough (WBT):** The pressure under which the first sign of water penetration through the porous laminate appears. The method used in the following examples uses a rate of pressure rise of 1 kg/cm<sup>2</sup> min.

**Cloud Point (CP):** The temperature at which the homogenous clear solution changes to hazy or cloudy solution upon cooling. The cloudy state indicates a phase separation process.

### EXAMPLE 1

A solution was made from 40 parts of a mixture of Resin F/HDDA/FX-13 at a ratio of 80/20/10 by weight, 53 parts M810, 7 parts BCA, 2 parts Irgacure 651 photoinitiator and 0.25 parts DC193 surfactant by mixing at 60°C.

The solution was coated on release paper with a wire wound rod (R.D. Specialities Rod #70) giving a wet film thickness of 130 microns. The coated paper was passed on a carrier belt at 10.5 meters/min. under a single 200 watt/inch Hanovia medium pressure mercury lamp equipped with an elliptical reflector. The reflector was situated at a distance of 100mm above the plain of the carrier belt. The lamp intensity was attenuated by means of a neutral density filter in such a manner that it produced a flux of effective UV radiation of 1.18 watt/cm as measured by an International Light IL745 Radiometer with A309 Light Bug which has a maximum sensitivity of 350nm. The precured coating was covered with a sheet of 0.3 oz/sq. yd. Cerex. The laminate was gently pressed with a roller and passed twice more through the same UV oven but without the metal screen so that the energy flux at each pass was 4.5 watt/cm. The laminate was removed from the release paper, washed thoroughly in a series of 4 baths with FREON 113 and then dried out at room temperature. The air flow and bubble point of the laminate were measured. The film was stripped off of the support and tested again. The void volume of the free film was also measured by weighing the free film before and after immersion in kerosene. The void volume was calculated from the known weights of the polymer and the kerosene and their



known densities (1.2 and 0.79 respectively). The results of these tests appear in Table 4.

#### EXAMPLE 2

The same solution as in Example 1 was coated and cured through the same schedule of steps except that no support was laminated to the membrane. The unsupported film was tested as in Example 1 and the results are given in Table 4.

The unsupported film has lower void volume due to a higher degree of shrinkage which is a result of the absence of a support. The drop in air flow follows this change in void volume.

#### EXAMPLE 3

A solution composed of:  
35 parts mixture of Resin F/HDDA 80/20 by weight  
56 parts M810  
9 parts BCA  
2 parts Irgacure 651  
0.5 parts DC193

was prepared as in Example 1. A series of coatings were made on release paper with WWR #40 (wet thickness 75 microns) and subjected to different levels of exposure. The various samples were then laminated to Hollytex 3254 and postcured twice as in Example 1. In the extreme case the light dose was zero. That is, no pre-exposure was made prior to lamination. On the other extreme a light dose of 2.0 watt/cm was applied prior to lamination and postcure. Samples of the precured layer were analyzed by gas chromatographic technique and the residual HDDA monomer was detected. Figure 6 shows the air flow properties of the membranes, after washing with FREON 113, as a function of the percent of the polymerized HDDA and as a function of light dose (Joule/cm<sup>2</sup>). Higher air flow characterized the higher precured samples. All precured samples exhibited higher air flow than that in which direct transfer coating (zero precure dose) was applied.

#### EXAMPLE 4

40 grams of solution containing 90 parts resin D, 10 parts N-Vinylpyrrolidone, 25 parts HDDA and 12.5 parts FX-13 was dissolved in a mixture of 57 grams M810 and 8 grams BCA. 2 grams Irgacure 651 and 0.25 grams DC193 were added. The final solution had a cloud point of above 20°C. It was coated with WWR #40 (75 micron wet thickness) on release paper and passed at 10 m/min under a UV lamp with metal screen attenuator such that the light flux was 1.18 watt/cm. A sheet of Hollytex 3254 nonwoven was laid and pressed gently over the precured film and the laminate was subjected to two more passes at 10 m/min under the non-attenuated light source. The film was washed with FREON 113 and dried as in Example 1. It had an air flow of 943 ml/min at 80cm H<sub>2</sub>O pressure on 2.5 diameter membrane disc. Its bubble point in kerosene was 1.58 bar and it had a WBT of 3.5kg/cm<sup>2</sup>.

#### EXAMPLE 4A

35 parts of resin D/HDDA/AA at a ratio of 81/9/10, 45.5 parts M810, 19.5 parts M12, 2 parts Irgacure 651 and 1 part DC193 were mixed. The solution had a cloud point of 21.5°C. It was coated with rod #50 (95 microns) on release paper and precured at 10 m/min with a fully powered lamp (4.5 watt/cm effective radiation flux). A sheet of Cerex 0.85 was laid and pressed gently onto it. The laminate was postcured twice more under the above radiation conditions. The washed and dried sample had an air flow of 1670 ml/min and a bubble point of 2.6 bar. The membrane was instantaneously wettable by water and had excellent wicking by water.

#### EXAMPLE 5

Thirty five (35) parts of a solution of Resin B (1.71%N) and HDDA in a ratio of 70/30 was mixed with 25.8 parts BCA and 39.2 parts M810. 2 parts Irgacure 651 and 0.5 parts L-540 surfactant were added. The cloud point of the solution was about 25°C. The solution was coated with WWR #60 (wet thickness of 115 microns) on a release paper and cured at 10 m/min with a light intensity of 4.5 watt/cm, laminated to Cerex 0.5 oz/sq.yd. and postcured twice at 10 m/min with a full powered lamp (4.5 watt/cm). The film was washed and dried as in Example 1. The resulting film was transparent and nonporous as detected by air flow measurements.

#### EXAMPLE 6

A solution of Resin B (1.71%N) and Resin J (6.16%N) in a ratio of 65.45/4.55 having an average %N = 2.0 was mixed with HDDA at a ratio of 70/30. 35 part of the above mixture were mixed with 18.8 parts BCA and 46.2 parts M810. Photoinitiator and surfactant were added as in Example 5. The cloud point of the solution was 25°C. The curing was done under similar conditions to those in Example 5. The washed and dried film (as in Example 1) was opaque white with an air flow of 1420 ml/min and BP of 0.83 bar.

#### EXAMPLE 6B

40 parts of the same composition of resins and HDDA as in Example 6, and the same photoinitiator and surfactants were mixed with 60 parts of M810/BCA such that a cloud point of 25°C was achieved, and were cured under the same conditions as in Example 6. It produced a transparent, nonporous film after washing and drying as in Example 1.

## EXAMPLE 7

35 parts of a solution of Resin B and HDDA in a ratio 50/50 was mixed with 16.1 parts BCA and 43.9 parts M810. 2 parts Irgacure 651 and 0.5 parts L-540 surfactant were mixed in at 60°C. The solution had a cloud point of 24.6°C. It was coated as detailed in Example 1 with WWR # 50 (95 micron wet thickness) at a speed of 2 m/min. The precure light intensity was set at 3 watt/cm by switching the lamp to half power. The precured coating was laminated to Hollytex 3254 and postcured at 2 m/min at full lamp intensity (4.5 watt/cm). The film was washed and dried as in Example 1. It had an air flow of 1400 ml/min and kerosene bubble point at 1.3 bar.

## EXAMPLE 8

35 parts of a solution of resin B, BCEA and HDDA in a ratio of 61.4/8.6/30 was mixed with 16.7 parts BCA and 47.3 parts M810. 2 parts Irgacure 651 and 0.5 parts L-540 was added. The solution had a cloud point of 25°. It was coated with WWR # 50 (wet thickness of 95 microns) precured at 10 m/min with 4.5 watt/cm UV lamp, laminated to Hollytex 3254 and postcured twice more under the same conditions. The film was washed and dried as in Example 1 and had an air flow of 1150 ml/min and kerosene bubble point of 0.8 bar.

## EXAMPLE 9

A mixture of 59 parts resin A (1.58%N) and 11 parts resin J (6.15%N) having an average %N = 2.3 was mixed with 30 parts HDDA. 35 parts of that mixture was mixed with 31.5 parts BCA and 33.5 parts M810. 2 parts Irgacure 651 and 0.5 pph L-540 were mixed in. Cloud point temperature was 25.5°C. The membrane was produced as in Example 6. The resulting laminate had an air flow of 1578 ml/min and a bubble point of 0.9 bar.

## EXAMPLE 9B

A similar composition to Example 9 but with average %N of 2.0% produced under similar conditions a transparent nonporous film.

## EXAMPLE 10

The same composition as in Example 9, but with a ratio of BCA/M810 32.7/32.3 and a cloud point of 19.8°C gave a white film with an airflow of 168 ml/min and a bubble point of 1.35 bar.

## EXAMPLE 10B

A solution was made of 35 parts resin J (6.16%N), 19.4 parts isopropylmyristate, 45.6 parts methyl laurate, 2 parts Irgacure 651, 0.4 parts DC193 and 0.1 parts L-540. It had a cloud point of 18.3°C. The solution was coated at 95 microns wet thickness on a release paper and precured at 7 m/min with half powered lamp attenuated with a metal screen and a tempered glass (radiation flux of 0.26 watt/cm) and laminated to a Cerex 0.5 oz./sq.yd. and postcured twice at above speed with full powered lamp.

The membrane, after washing and drying as in Example 1, gave a rather rigid coating with air flow of 530 ml/min and bubble point at 3.67 bar.

## EXAMPLE 11

A solution containing 35 parts of a mixture of Resin D/HDDA/FX-13 in a ratio of 72/28/10 was mixed with 65 parts M810, 2 parts Irgacure 651 and 0.5 parts DC193. The solution was coated to 95 microns wet thickness with WWR # 50 and cured in air at 5 m/min with full lamp intensity such that a light dose of 0.54 joule/cm<sup>2</sup> was received. The cured coating was laminated to Cerex 0.5 oz./sq.yd. and postcured twice under the same conditions. The film, after being washed and dried, showed good adhesion between the porous membrane and the fabric.

## EXAMPLE 12

An experiment similar to Example 11 was done with the main difference being that the precure stage was done under a nitrogen atmosphere. The light intensity was reduced by increasing the speed to 14 m/min and decreasing the lamp power to 1/2 intensity such that the total light dose was 0.13 joule/cm<sup>2</sup>. The degree of curing as judged by the mechanical integrity of the precured film and its opaqueness was 7 on a scale of zero to 10 and considerably lower than the grade of 9 given to the precured stage of the film of Example 11. The adhesion to the Cerex substrate was nevertheless much poorer.

SEM pictures (Figures 7 and 8) show that the air cured sample of Example 11 has a semi-fused sticky layer at the polymer/air interface. This layer wets out the fiber and adheres to it. No such layer exists in the nitrogen cured samples of Example 12 (Figures 9 and 10).

## EXAMPLE 13

A solution containing 35 parts of a mixture of Resin D/HDDA/FX-13 in a ratio of 72/28/10 by weight, 64 parts M810, one part BCA and 0.5 parts DC193 was coated with WWR # 55 giving wet thickness of 100 microns on a release paper. The coating was passed through an electron beam source (Charmilles-ESI, Electro Curtain type) operated at 170 kilovolts under an inert nitrogen atmosphere at 30 m/min so that it was exposed to 0.25 MRAD. The resulting tacky film was laminated to Cerex 0.5 oz./sq.yd. and postcured with a dose of 3 MRAD. The laminate was washed in FREON and dried. Its properties are given in Table 5.

**EXAMPLE 13A**

A solution made of 35 parts of a mixture of resin D/HDDA/FX 13 in a ratio of 72/28/10 was mixed with 61.4 parts M810, 3.6 parts BCA and 0.5 parts L-540 and had a cloud point of 20°C. The solution was coated on a release paper and precured on an "Electro Curtain" pilot coating line of Energy Sciences Inc. (Woburn, Mass.) using 0.5 MRAD electron beam dose under ambient atmosphere at 40 ft/min. The precured coating was then laminated to 0.8 oz., spunbonded polypropylene nonwoven which was previously corona treated with 6.5 watts-min. per foot and also electron beam treated in air with 5 MRAD. The laminated structure was then passed again through a 4 MRAD electron beam radiation under nitrogen at 20 ft/min and separated from the release paper. After being washed and dried, the product showed good adhesion of the coating to the support.

**EXAMPLE 13B**

The same experiment done with precuring under inert nitrogen atmosphere produced a coating that could not be transferred onto the support for lack of adhesion.

**EXAMPLE 14**

A solution containing 35 parts of a mixture of Resin D/HDDA/FX-13 72/28/10 by weight, 63 parts M810, 2 parts BCA, 2 parts Irgacure 651 and 0.5 parts DC193 was coated on a release paper to a thickness of 75 microns, passed at 10 m/min under a partially screened UV lamp with a radiation flux of 1.18 watt/cm. The partially cured film was laminated to an industrial wiping paper (made by Hogla, Israel) and postcured twice under a full intensity lamp. The laminate was washed in FREON 113 and dried out. The resultant laminate is an opaque white smoothly coated paper with very good flexibility and good hand feel. Its properties are given in Table 5.

**EXAMPLE 15**

A solution containing 35 parts of Resin D/HDDA/FX-13 at a ratio of 81/19/10 by weight, 58.9 parts M810, 6.1 parts BCA, 2 parts Irgacure 651 and 0.5 parts L-540 had a cloud point of 19.2°C. The solution was coated on a continuous line equipped with one 200 W/IN lamp for the precure stage and two 200 W/IN lamps for the final cure. The lamination of the fabric to the precured coating was done between the first two lamps. Separation of the coated fabric from the release paper was done on two separate rewind stations at the exit from the third lamp. FREON washing of the coating fabric was then proceeded on a separate multi-step washing machine operated at 2 meters per minute.

The solution was coated on the release paper by means of WWR #55 so that 100 microns of wet thick film was laid down and cured at 7 m/min. The precure intensity was attenuated using a half power lamp with a metal screen and 5mm tempered glass so that a total energy flux of 0.30 watt/cm was used. The precured solution was laminated to a woven nylon fabric which had a light transmittance of 2% in the sensitivity region of the International Light's Light Bug indicator (350nm). Postcuring was done with two fully powered lamps. The resulting washed fabric had an opaque white coating on one side and its original deep violet color on the other side. The coated fabric had good flexibility and feel. Its properties are given in Table 5.

**EXAMPLE 16**

A solution made of 35 parts mixture of Resin D/HDDA/FX-13 at a ratio of 72/28/10, 62 parts M810, 3 parts BCA, 2 parts Irgacure 651 and 0.5 parts L-540 had a cloud point of 19.3°C. The solution was applied on a release paper with WWR #70 giving a wet thickness of 130 microns. It was precured at 7 m/min with a radiation flux of 0.33 watt/cm achieved by metal screen and tempered glass filters. The precured coating was laminated to a 0.8 oz. spunbonded polypropylene nonwoven which was freshly treated with a corona discharge of 2.5 joule/cm<sup>2</sup> prior to the lamination. The laminate was postcured twice at the same speed through a full intensity lamp. The laminate was washed in FREON 113 and dried out. It had good adhesion between the coating and the fabric but a high tendency to crack parallel to the machine direction of the fabric. The laminate had good air flow (Table 5) but zero bubble point due to defects.

**EXAMPLE 17**

An experiment similar to that of Example 16, but with a formulation identical to that used in Example 15, gave very poor adhesion of the membrane to the support. The membrane, which was practically unsupported, gave a low air flow (Table 5), but a good bubble point and had good mechanical strength including the cross machine direction.

**EXAMPLE 18**

A solution made of 35 parts mixture of Resin D/HDDA/FX-13 at a ratio of 72/28/10, 38.6 parts methyl laurate, 26.4 parts BCA, 2 parts Irgacure 651, 0.4 parts DC193 and 0.1 parts L-540 had a cloud point of 22.3°C. The solution was coated on the coating line which is described in Example 15. A 75 micron thick wet film was applied on a release paper and passed at 7 m/min through a first lamp attenuated with screens to produce a light flux of 0.32 watt/cm and laminated to a 0.8 oz./sq.yd. spunbonded polypropylene nonwoven which was treated on-line with a 25 watt/cm corona discharge to promote adhesion. The laminate was continuously

pulled through two fully powered lamps and separated from the release paper.

A second coating of the same thickness and composition was applied on a release paper and precured as before except that an attenuated light intensity of 0.72 watt/cm was used. The coated side of the above laminate was laminated to this second layer such that a double coating porous film was attached to the fabric. This composite structure was postcured as before, separated from the release paper, washed in FREON 113 and dried out. In this example the first coating, which was only slightly precured, penetrated within the fiber structure of the fabric and produced good anchoring to it. This coating, which was still very defective, was then laminated to a better precured layer that covered the whole structure with a nondefective layer. The composite structure had fair strength in the so called machine direction of the fabric but the membrane had a high tendency to crack upon slight cross-web extension. The other properties are given in Table 5.

#### EXAMPLE 19

The same experiment as in Example 18 was done except that the second coating had a composition of 35 parts Resin D/HDDA/FX-13 at a ratio of 81/19/10, 37.2 parts methyl laurate, 27.8 parts BCA 2 parts Irgacure 651, 0.4 parts DC193 and 0.1 parts L540. It had a cloud point of 22.6°C. The resulting membrane had better resistance to cross machine deformations and less defects than samples of Example 18.

#### EXAMPLE 20

A solution containing 37.5 parts of a mixture of 76.5/23.5/8.5 of Resin D/HDDA/FX-13, 59 parts M810, 3.5 parts BCA, 2 parts Irgacure 651 and 0.5 parts L-540 had a cloud point of 16.3°C. The solution was applied with WWR #55 (wet thickness of 100 microns) on a release paper and cured on the continuous line of Example 15 with precure intensity of 3.36 watt/cm (half intensity lamp, no filters) at a speed of 10 m/min. The coated paper was laminated on 0.6 oz. Cerex, postcured and processed as in Example 15. The resulting membrane had excellent mechanical properties. No defect in the coating had been noticed by pulling the fabric to its break point. However, the coating suffered from partial blocking which caused partial delamination in certain spots.

#### EXAMPLE 21

A similar solution to that of Example 20, but with 61.5/1.0 ratio of M810/BCA and surfactants 0.4/0.1 parts DC193/L-540 so that the cloud point was 16°C, was coated with WWR #30 (55 microns) and processed as in Example 20. A second coating made of 30 parts of a mixture of resin D/HDDA/FX13 at a ratio of 63/37/10 with 68.7/1.3 parts M810/BCA, 2 parts Irgacure 651, 0.4 parts DC193, 0.1 parts L540 and having a cloud point of 21.6°C was applied with a WWR #18 (35 microns) on a release paper and laminated to the coated fabric under the same precure conditions as in the first coating and with a similar procedure as in Example 18. The resulting washed and dried film had similarly good mechanical behavior as the single coating of Example 20, but had no defects due to blocking.

#### EXAMPLE 22

The membrane side of a sample of Example 20 was thinly sprayed with a solution of a commercial rubber cement in petroleum distillate and immediately laminated to another layer of a thin 0.3 oz./sq.yd. Cerex by means of a squeeze roll. The three ply laminate had excellent surface texture and scratch resistance. The sample retained the typical characteristics of the breathable laminate (See Table 5).

#### EXAMPLE 23

A solution made of 35 parts Resin D/HDDA/FX-13 in a ratio of 72/28/10, 64 parts M810, one part BCA, 2 parts Irgacure 651 and 0.5 parts L-540 had a cloud point of 20.7°C. The solution was coated with WWR #30, wet thickness of 55 microns, precured at 10 m/min with a radiation flux of 1.18 watt/cm and laminated to 0.4 oz./sq.yd. Cerex and postcured once with a full powered lamp at 10 m/min. Two such laminates with the membrane face to face were pressed together with a roller and postcured twice more under the same conditions. The resultant laminate after being washed and dried showed good adhesion between the layers and excellent surface texture and scratch resistance, yet, it kept the good flow properties of similar nonsandwiched coatings.

#### EXAMPLE 24

This example has the same composition and the same thickness as in Example 23 and was precured at 5 m/min with 4.5 watt/cm radiation flux and laminated to 0.3 oz./sq.yd. Cerex. The membrane side of the laminate was recoated with 20% solids solution containing 20 parts Resin D/HDDA/FX13 in a ratio of 72/28/10, 72 parts M810, 8 parts BCA, 2 parts Irgacure 651 and 0.5 parts L540. The solution had a cloud point of 23°C. The coating was applied with WWR #30. It was covered with another sheet of Cerex of the same weight and cured twice at 10 m/min with a full intensity lamp. The washed and dried laminate had good uniformity and adhered well to both substrates.

#### EXAMPLE 25

A solution was made with 35 parts of Resin D/HDDA/TPGDA/FX-13 72/8/20/10, 1.7 parts BCA, 63.3 parts M810, 2 parts Irgacure 651 and 0.5 parts L-540. It had a cloud point of 23°C. The solution was coated and cured at 10 m/min at 100 micron wet film thickness and with nonattenuated lamp. 0.5 Cerex was laminated to the

coating and the laminate was postcured twice under similar conditions and washed and dried. Its properties are given in Table 5.

**EXAMPLE 26**

A solution made of 35 parts Resin D/HDDA/FX-13 72/28/10, 22 parts DBE-5, 43 parts methyl laurate, 2 parts Irgacure 651 and 0.5 parts L-540 had a cloud point of 25.8°C. It was coated 100 microns thick and precured at 10 m/min under full powered lamp, laminated to Cerex 0.5 and postcured twice more. The washed and dried membrane had the properties as shown in Table 5.

**EXAMPLE 27**

A solution containing 35 parts of 70/30 ratio of Resin K/HDDA, 65 parts methyl myristate, 2 parts Irgacure 651 and 0.5 parts L-540 had a cloud point of 24.2°C. The solution was coated 95 microns thick on a release paper, precured at 10 m/min with half powered lamp and laminated to Hollytex 3254. The laminate was postcured twice, washed and dried. It had low air flow and a high bubble point which indicates a tendency to collapse. It was brittle at the point of pleating and therefore non-suitable for coated fabrics.

**EXAMPLE 28**

A similar coating based on 35 parts of Resin L/HDDA in a ratio of 70/30, 9.9 parts isopropylmyristate, 55.1 parts isopropylpalmitate, 2 parts Irgacure 651 and 0.5 parts L540 and a cloud point of 25°C was similarly laminated to Cerex 0.85 oz./sq.yd. It produced similar results to that of the previous example and a similarly brittle product.

**EXAMPLE 29**

A solution made of 35 parts Resin C/HDDA/FX-13 in a ratio of 80/20/7 was mixed with 50 parts M810, 15 parts BCA, 2 parts Irgacure 651, 0.4 parts DC193 and 0.1 parts L-549 had a cloud point of 18.4°C. The solution was coated and processed as in Example 1 using a coating thickness of 95 microns (Rod #30), speed of 10 m/min, Hollytex 3256 support and precure intensity of 1.18 watt/cm. The resulting laminate had an opaque white smooth coating of good flexibility and handling characteristics. It had an air flow of 990 ml/min, kerosene bubble point of 2.79 bar, and water breakthrough of 1.75 kg/cm<sup>2</sup>.

**EXAMPLE 30**

A similar solution was made with Resin G replacing Resin C and a mixture of 36 parts M810 and 29 parts methyl laurate as solvents, such that the cloud point was 19.0°C. It was coated and processed as in Example 29 except that the precure intensity was 2.96 watt/cm. The resulting laminate had a similar appearance and mechanical characteristics. It had an air flow of 1140 ml/min, kerosene bubble point of 2.51 bar, and water breakthrough of 1.75 kg/cm<sup>2</sup>.

**EXAMPLE 31**

A similar composition to that of Example 29 but with Resin I replacing Resin C and with a mixture of 51.1 parts M810 and 13.9 parts BCA had a cloud point of 21.8°C. The solution was coated and processed as in Example 29. The resulting film similarly had good mechanical properties and good appearance. It had an air flow of 100 ml/min., kerosene bubble point of 7.0 bar and water breakthrough of 5.5 kg/cm<sup>2</sup>.

**EXAMPLE 32**

A solution was made with 35 parts of resin E/HDDA/TOCTAM in a ratio of 80/20/20, 60 parts DIBA, 5 parts DIOA, 2 parts Irgacure 651, 0.4 parts DC193 and 0.1 parts L-540. The solution was coated and processed as in Example 30. The resulting film had good mechanical behavior. It had an air flow of 780 ml/min, kerosene bubble point of 3.13 bar and water breakthrough of 3.0 kg/cm<sup>2</sup>.

**EXAMPLE 33**

An unsupported porous membrane was made by making a solution of 25 parts Resin M/HDDA 70/30 with 54.4 parts M810, 0.6 parts BCA, 2 parts Irgacure 651 and 0.5 parts DC193. The solution was coated and processed as in Example 2. The washed and dried film was opaque white with good handling characteristics. It had a void volume of 52.9%, a kerosene B.P. of 3.2 bar and an air flow of 500 ml/min for sections 100 microns thick. (Table 6)

**EXAMPLE 34**

An unsupported porous film was made similar to Example 33 but with 40 parts Resin F/BDDA 80/20 mixture and 57.5/2.5 ratio of M810/BCA. The resulting membrane had an air flow of 622 ml/min and a kerosene B.P. of 2.0 bar. (Table 6)

**EXAMPLE 35**

An unsupported membrane was made similar to Example 33 but with 45 parts Resin F/HDDA 80/20 and 55 parts of M810 gave a white and flexible film with a kerosene B.P. of 2.7 bar and air flow of 407 ml/min. (Table 6)

## EXAMPLE 36

A similar membrane to that in Example 35 but with HDDA substituted by PEA produced a more flexible membrane with a kerosene B.P. of 4.7 bar and air flow of 266 ml/min. (Table 6)

## 5 EXAMPLE 37

A solution was made of 40 parts Resin E/HDDA 80/20, 48 parts M810, 12 parts BCA, 2 parts Irgacure 651 and 0.5 parts DC193. The solution was hazy but stable at room temperature. The solution was coated with WWR #70 on a release paper and cured twice with a full powered 200 w/inch lamp (4.5 watt/cm effective intensity) at 10 m/min, removed from the release paper, washed and dried. The resulting membrane had good strength and handling characteristics with a void volume of 57.7%, air flow of 560 ml/min, and kerosene bubble point of 1.93 bar. (Table 6)

## EXAMPLE 38

The same solution as in Example 37 was centrifuged. The solution became clear and a fraction of 6% of the solution was found as a viscous heavier layer. The layer was analyzed to be a higher molecular weight fraction of the resin. The clear fraction was coated and processed as above. The resulting porous film had similar handling and mechanical characteristics with similar flow properties with air flow of 550 ml/min. A kerosene bubble point of 1.71 bar and a void volume of 57.2%. (Table 6)

## 20 Example 39

A solution composed of 35 parts of Resin D/HDDA/FX-13 in a ratio of 72/28/10, 62 parts M810, 3 parts BCA, 2 parts Irgacure 651 and 0.5 parts L-540 was coated with WWR #55 (wet thickness 100 microns) on a release paper at 7m/min. The coating was precured with half powered lamp (3.36 watt/cm), laminated to Cerex 0.6 oz. and postcured through two fully powered lamps on a continuous coating and laminating line. The washed and dried sample had good flexibility, handability and water repellency. Its flow properties are given in Table 7.

## Example 40

A solution composed of 35 parts Resin D/HDDA in a ratio of 63/37, 57 parts M810, 8 parts methyl laurate, 2 parts Irgacure 184, 0.1 parts L-540 and 0.4 parts DC193 was coated and processed as in Example 1 except that a precure intensity of 1.94 watt/cm was employed using a fully powered lamp attenuated with a metal screen. The resultant laminate was instantaneously wettable (see Table 7)

## Example 41

A sample of laminate from Example 40 was immersed in a solution of a perfluoro, water repellent polymer, FC-725 (a product of 3M). The solution was made into 1% solids solution in Freon 113 by first stripping off the original butyl acetate solvent in the original FC-725 product and redissolving it in the Freon solvent. The impregnated laminate was allowed to dry out and tested for its flow properties and hydrophobicity. The impregnation caused a partial loss of flow properties and a moderate level of hydrophobicity as judged by the water breakthrough pressure of 0.9 kg/cm<sup>2</sup>.

## Example 42

The same as Example 41 except that 2% solids FC-725 solution was used for impregnation. Air flow dropped and water breakthrough increased to 1.5 atm.

## 45 Example 43

A solution composed of 50 parts of Resin F/HDDA 85/15, 50 parts M810, 2 parts Darocur 1116 and 0.4 parts FC-430 was coated on a siliconized polyester sheet with WWR #70 (130 microns wet thickness). The coating was cured by passing three times under a fully powered lamp at 8 m/min. The unsupported membrane was removed from the carrier sheet and washed thoroughly in Freon. The resulting membrane had good strength and flexibility. It had a void volume of 46%, kerosene bubble point of 36 psi and air flow of 45 ml/min cm<sup>2</sup> at 80cm water pressure. It was instantaneously wettable.

## Example 44

The above unsupported membrane was impregnated with 0.6% FC-725 solution in Freon as in Example 41. Air flow dropped to 28 ml/min cm<sup>2</sup> and the membrane was still instantaneously wettable.

## Example 45

The same as above but with 1% FC-725. Air flow dropped to 18 ml/min cm<sup>2</sup> and the membrane was still slowly wettable.

## Example 46

The same as above with 2% FC-725. Air flow dropped to lower than 2 ml/min cm<sup>2</sup>. The membrane was very slowly wettable.

**Example 47**

Similar impregnation with Zonyl TBC, an ester derivative of a perfluoro alkanol made by DuPont, at 1% solids in FREON 113 lowered air flow down to 30 ml/min cm<sup>2</sup> and the membrane was still slowly wettable.

**Example 48**

Similar impregnation with 2% Zonyl TBC reduced air flow to 6.6 ml/min cm<sup>2</sup> and the membrane was very slowly wettable.

**Example 49**

A solution composed of 35 parts Resin D/HDDA/FX-13 at a ratio of 72/28/10, 63 parts M810, 2 parts Irgacure 651, 0.1 parts L-540 and 0.4 parts DC193 which had a cloud point of 19.3°C coated 95 microns thick at 10 m/min at full lamp intensity, laminated to Cerex 0.5 and post cured twice under similar conditions. The washed and dried sample had good flow properties, good mechanical strength and flexibility and very good water breakthrough and a very low percent of water gain upon 24 hours exposure to water.

**Example 50**

A similar composition as Example 49 was produced under similar conditions but with TOCTAM instead of FX-13 and a ratio of 53/12 of M810/methyl laurate as solvents such that the cloud point was 20.7°C and the membrane had moderate hydrophobicity.

**Example 51**

A membrane as prepared in Example 49 but with a ratio of 72/28/20 of Resin D/HDDA/TOCTAM (higher level of TOCTAM) and a solvent composition of 47/18 of M810/methyl laurate. The formulation had a cloud point of 19.7°C and the resultant membrane had good flow and hydrophobic characteristics.

**Example 52**

A similar composition to that of Example 49 but with laurylacrylate (LA) instead of FX-13 and 4/61 parts of BCA/M810 as the solvent. The solution had a cloud point of 20.2°C and the resultant membrane had moderate flow and hydrophobic properties.

**Example 53**

A similar composition to that prepared in Example 52 but with a 72/28/20 ratio of Resin D/HDDA/LA and 8/57 parts BCA/M810 as the solvents. A cloud point of 21°C was determined. This composition produced a transparent nonporous coating.

**Example 54**

A membrane as prepared in Example 49, but with a 81/19/20 ratio of Resin C/HDDA/TOCTAM and a solvent ratio of 49.4/15.6 of M810/M12. The formulation had a cloud point of 20°C. It was coated in the same way as Example 49 except that Cerex 0.85 oz. was used. The resultant membrane had good flow and hydrophobicity and very good mechanical properties. It had an extensibility of 35% before the appearance of holes in the coating.

**Example 55**

A solution was made with 40 parts Resin F/HDDA/FX189 in a ratio of 90/10/7 and with 48 parts M810, 12 parts BCA, 2 parts Irgacure 651, 0.4 parts DC193 and 0.1 parts L540. The solution had a cloud point of 20.4°C. The solution was coated 95 microns thick at 7 m/min under a full lamp intensity, attenuated with a metal screen to effective intensity of 0.44 watt/cm. The precured membrane was laminated to Hollytex 3256 support and postcured twice under similar conditions. The resulting film had good mechanical and handling characteristics and properties as detailed in Table 7.

**Example 56**

A membrane was made as in Example 55 but with FC5165 substituting for FX189 and with solvent composition of 47 parts M810, 13 parts BCA, 2 parts Irgacure 651, 0.4 parts DC193 and 0.1 parts L540. The solution had a cloud point of 20.1°C. The resulting membrane had good mechanical and handling characteristics with properties as detailed in Table 7.

**Example 57**

A solution was made with 40 parts resin F/HDDA/FX13 at a ratio of 80/20/3 and with 52 parts M810, 8 parts BCA, 2 parts Irgacure 651, 0.4 parts DC193 and 0.1 parts L540. The solution had a cloud point of 19.8°C. The solution was coated 95 microns thick at 10 m/min at half lamp intensity laminated to Hollytex 3256 support and postcured twice at the same speed under full lamp intensity. The washed and dried samples had good flow and mechanical properties. The properties are detailed in Table 7.



## Example 58

A solution made of 40 parts Resin F/HDDA/FX13 at a ratio of 80/20/25, a solvent composition of 45.2 parts of M810 and 14.8 parts of BCA, 2 parts Irgacure 651, 0.4 parts DC193 and 0.1 parts L540 had a cloud point of 20.9°C. The solution was used to make a membrane under the same conditions of Example 57. The washed and dried samples had good flow, mechanical and hydrophobic properties as detailed in Table 7.

## Example 59

A solution was made with 35 parts Resin D/HDDA/TOCTAM in a ratio of 81/19/50 and with 32.2 parts M810, 32.8 parts M12, 2 parts Irgacure 651, 0.4 parts DC193 and 0.1 parts L540. The solution had a cloud point of 20.4°C. It was coated 95 microns thick at 7 m/min at half lamp intensity, laminated to Cerex 0.85 and postcured twice under full lamp intensity at a similar speed. The washed and dried samples had low flow properties, high bubble points and high water breakthrough as detailed in Table 7.

## Example 60

A solution was made as in Example 55, but with FX14 substituting for FX189 and with solvent composition of 11.9 parts BCA, 48.1 parts M810, 2 parts Irgacure 651, 0.4 parts DC193 and 0.1 parts L540. The solution had a cloud point of 19.4°C. The solution was used to make a membrane under the same conditions of Example 55. The resulting membrane had good mechanical and handling characteristics with properties as detailed in Table 7.

## Example 61

A solution composed of 40 parts Resin D/HDDA/TOCTAM/FX13 at a ratio of 72/28/18/2, 20.8 parts M12, 39.2 parts M810, 2 parts Irgacure 651 and 0.5 parts L-540 had a cloud point of 22.8°C. It was used to make a coated laminate as in Example 49. The coated laminate had good mechanical and handling properties. Its other properties are given in Table 7.

The invention has been described in an illustrative manner, and it is to be understood that the terminology which has been used is intended to be in the nature of words of description rather than of limitation.

Obviously, many modifications and variations of the present invention are possible in light of the above teachings. It is, therefore, to be understood that within the scope of the appended claims wherein reference numerals are merely for convenience and are not to be in any way limiting, the invention may be practiced otherwise than as specifically described.

TABLE 1 ACRYLATED URETHANE OLIGOMERS

RESIN	M <sub>n</sub> <sup>(1)</sup>	Function- ality	$\bar{X}_n$ <sup>(2)</sup>	R <sub>1</sub> <sup>(3)</sup>	R <sub>2</sub> <sup>(4)</sup>	R <sub>3</sub> <sup>(5)</sup>
A	3500-4500	2	1.58	HPA	TDI	EG-ADA
B	3000-3500	2	1.71	HPA	IPDI	EG-ADA
C	1200 <sup>(6)</sup>	3	-	HEA	(6)	PCL
D	2000	2	3.78	HEA	IPDI	BD-ADA
E	1200-1400	2	4.16	HEA	HMDI	EG-ADA
F	1200-1400	2	4.35	HEA	IPDI	EG-ADA
G	1200-1400	2	4.50	HEA	IPDI	PCL
I	1700-2000	2	5.03	HEA	IPDI	BD-ADA
J	442	2	6.16	HEA	TMDI	-
K	1500	2	4.8	HEA	TDI	PPG
L	1500	2	4.36	HEA	IPDI	PPG
M	1200	2	4.67	HEA	IPDI	DEG-ADA

## Footnotes for Table 1:

- (1) M<sub>n</sub> is the number average molecular weight based on the stoichiometry of the building blocks, R<sub>1</sub>, R<sub>2</sub> and R<sub>3</sub>.
- (2)  $\bar{X}_n$  based on elemental microanalysis.
- (3) HEA is 2-hydroxyethylacrylate, HPA is 2-hydroxy propyl acrylate
- (4) IPDI is 3-isocyanatomethyl-3,5,5-trimethylcyclohexyl-isocyanate, also known as isophorone diisocyanate. TDI is mixed isomers of toluenediisocyanate. HMDI is methylene bis (4-cyclohexylisocyanate) also known as hydrogenated methylenedianiline diisocyanate.
- (5) EG-ADA is the repeat unit of the polyester polyol based on the condensation product of ethylene glycol and adipic acid. DEG-ADA is the repeat unit of diethyleneglycol and adipic acid. BD-ADA is the repeat unit of polyester polyol based on the condensation product of 1,4 butanediol and adipic acid. PCL is the repeat unit of polycaprolactone diol. PPG is the repeat unit of Polypropyleneglycol. TMDI is mixed isomers of trimethylhexamethylene diisocyanate.
- (6) Commercial resin made by H. Rahn, Zurich from a proprietary aliphatic trifunctional isocyanate

TABLE 2 - LIST OF MATERIALS AND ABBREVIATIONS USED IN THE EXAMPLES

## Reactive Dilluents

BDDA - 1,4 butanediol diacrylate

5 HDDA - 1,6 Hexanediol diacrylate

TPGDA - tripropylene glycol diacrylate

TMPTA - trimethylopropane triacrylate

PEA - phenoxyethylacrylate

BCEA - butylcarbamyethylacrylate (adduct of butyl isocyanate and hydroxyethylacrylate)

10 AA - Acrylic acid

## Hydrophobic Monomers

FX-13 - 2-(N-ethylperfluoro octane sulfonamido) ethylacrylate, a product of 3M

FX-14 - Essentially 2-(N-ethylperfluoro octane sulfonamido) ethyl methacrylate. A product of 3M Corp.

15 FX-189 - Essentially 2-(N-butylperfluoro octane sulfonamido) ethylacrylate. A product of 3M Corp.

FC-5165 - 1,1-dihydro perfluoro octulacrylate  $\text{CF}_3(\text{CF}_2)_8\text{CH}_2\text{OCOCH}=\text{CH}_2$ 

TOCTAM - N-1,1,2,2, tetramethylbutylacrylamide, (Tertiary octylacrylamide) a product of National Starch and Chemical Corp.

20 TABLE 2 - Continued

## Solvents

M810 - Commercial mixture containing approximately 55% methyl caprylate, 40% methyl caprate, 3% methyl caproate and 2% methyl laurate.

25 BCA - butyl cellosolve actuate (butyl glycol acetate)

M12 - methyl laurate

DIBA - diisobutyladipate

DIOA - diisooctyladipate

DBE-5 - Commercial solvent by DuPont containing dimethylglutarate as the main constituent.

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## MISCELLANEOUS COMPONENTS

Irgacure 651 - benzil dimethyl ketal. A photoinitiator made by Ciba Geigy.

DC193 - silicone surfactant. A product of Dow Corning.

L540 - silicone surfactant. A product of Union Carbide Corp.

35 FC430 - coating additive. A product of 3M Corp.

Irgacure 184 - 1-hydroxycyclohexylphenylketone. A product of Ciba Geigy.

Darocur 1116 - 1-(4-isopropylphenyl)-2-hydroxy-2methylpropan-1-one

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TABLE 3 List of Nonwoven Supports Used in The ExamplesSupports

BRAND NAME	PRODUCER TYPE	-----weight-----	
		(g/m <sup>2</sup> )	(oz./sq.yd)
CEREX 0.3	Monsanto polyamide spunbonded	10	0.3
CEREX 0.4	Monsanto polyamide spunbonded	14	0.4
CEREX 0.5	Monsanto polyamide spunbonded	17	0.5
CEREX 0.6	Monsanto polyamide spunbonded	20	0.6
CEREX 0.85	Monsanto polyamide spunbonded	29	0.85
Hollytex 3254	Eaton-Dikeman polyester spunbonded	63	-
Hollytex 3251	Eaton-Dikeman polyester spunbonded	17	0.5
Hollytex 3256	Eaton-Dikeman polyester spunbonded	25	0.75
Paper	Hogla paper, Industrial wiping grade	24	-
0.8 oz.	0.8 oz./sq.yd. spunbonded polypropylene	27	0.8

Table 4

Example #	Thickness of the unsupported film (microns)	Void volume (%)	Air flow (ml/min*)	Bubble point kerosene (atm)
1 (Laminate)	-		841	1.65
1 (Stripped off film)	104	64.4	808	1.60
2 (Unsupported)	104	57.9	448	1.60

\* Air flow is expressed in ml/min for a 2.5cm disc under a pressure differential of 80 cm of water.

TABLE 5

Ex	Support	Wet Film Thickness (microns)	Curing Speed (m/min)	Precure Dose (J/cm <sup>2</sup> )	Air Flow (ml <sub>2</sub> /min, 5cm disc @80cmH <sub>2</sub> O)	Kerosene Bubble Point (bar)	Water Break Thru (kg/cm <sub>2</sub> )	Extensibility* (%)	Adhesion (Tape peel test)
11	Cerex 0.5	95	5	0.54	900-1700	1.42	3	34.7	good
12	Cerex 0.5	95	14	0.13	1960	-	-	27.5	fair
13	Cerex 0.5	100	30	0.25MRAD	1476	1.97	3	22.8	fair
14	Paper	75	10	0.07	620	1.6	3.5	-	good
15	Woven nylon	100	7	0.026	254	-	3.5	-	fair
16	0.8 oz. polypropylene	130	7	0.028	1260	0	2	poor	good
17	0.8 oz polypropylene	130	7	0.08	200	2.35	Adhesion failure		poor
18	0.8 .oz polypropylene	45/45	7	0.028/ 0.062	1760	.68	0.8	-	good
19	0.8 oz. polypropylene	45/45	7	0.027/ 0.062	620	1.27	1.49	good	good
20	Cerex 0.6	100	10	0.20	660	2.2	4.5	excellent	good
21	Cerex 0.6	55/35	7	0.20	835	2.13	2.3	excellent	good
22	Cerex 0.6/ Cerex 0.3	100	10	0.20	766	2.65	2.5	good	good
23	Cerex 0.4/0.4	55/55	10	0.07	1020	1.25		excellent	good
24	Cerex 0.3	55/55	5/10	0.54	2080	0.75		excellent	good
25	Cerex 0.5	100	10	0.27	1670	1.2	3.0	good	good
26	Cerex 0.5	100	10	0.27	1876	2.1	3.5	good	fair
27	Hollytex 3254	95	10	0.18	440	4.35	-	brittle	good
28	Cerex 0.85	100	10	0.27	660	3.95	-	brittle	good
29	Hollytex 3256	95	10	0.07	990	2.79	1.75	excellent	fair
30	Hollytex 3256	95	10	0.18	1140	2.51	1.75	good	good
31	Hollytex 3256	95	10	0.07	100	7.0	5.5	excellent	good
32	Hollytex 3256	95	10	0.18	780	3.13	3.0	good	fair

\* % extension to the appearance of first hole in the membrane

TABLE 6

## Properties of Unsupported Membranes

Ex	Wet Film Thickness (microns)	Curing Speed (m/min)	Void Volume (%)	Air Flow (ml/min, 5cm <sup>2</sup> disc @80cmH <sub>2</sub> O)	Kerosene Bubble Point (bar)
33	100	10.5	52.9	500	3.2
34	100	10.5		622	2.0
35	100	10.5		407	2.7
36	100	10.5		266	4.7
37	130	10.0	57.7	560	1.93
38	130	10.0	57.2	550	1.71

Table 7

Example #	Polymer	Monomer Support	Precure dose <sup>2</sup> (J/cm <sup>2</sup> )	Impregnation Solution In Freon 113 Compound	Kerosene Bubble Point (psi)	Air Flow <sup>2</sup> (cc/min cm <sup>2</sup> 80cmH <sub>2</sub> O)	Water Break Through <sup>2</sup> (kg/cm <sup>2</sup> )	% Water Penetration*
39	Resin D/HDDA	FX-13 Cerex 0.5	0.20	-	22	375	3.0	
40	Resin D/HDDA	- Cerex 1.0	0.17	-	23	262	0.0	
41	Resin D/HDDA	- Cerex 1.0	0.17	FC-725	-	189	0.9	
42	Resin D/HDDA	- Cerex 1.0	0.17	FC-725	-	105	1.5	
42A	Resin F/HDDA	FX-13 Unsupported	-	-	33.7	86	2.5	
49	Resin D/HDDA	FX-13 Cerex 0.5	0.27	-	18	446	3.5	1.7
50	Resin D/HDDA	TOCTAM Cerex 0.5	0.27	-	18	506	1.5	Wettable
51	Resin D/HDDA	TOCTAM Cerex 0.5	0.27	-	18	476	2.0	11.7
52	Resin D/HDDA	LA Cerex 0.5	0.27	-	17	266	2.0	Wettable
53	Resin D/HDDA	LA Cerex 0.5	0.27	-	collapsed structure			
54	Resin D/HDDA	TOCTAM Cerex 0.85	0.27	-	29	250	2.17	
55	Resin F/HDDA	FX189 Hollytex 3256	0.04	-	31	200	2.0	
56	Resin F/HDDA	FC5165 Hollytex 3256	0.04	-	34	196	3.0	
57	Resin F/HDDA	FX13 Hollytex 3256	0.27	-	30	220	1.4	
58	Resin F/HDDA	FX13 Hollytex 3256	0.27	-	31	220	3.5	
59	Resin D/HDDA	TOCTAM Cerex 0.85	0.27	-	58	76	4.2	
60	Resin F/HDDA	FX14 Hollytex 3256	0.27	-	31	196	2.0	
61	Resin D/HDDA	FX13/ TOCTAM Cerex 0.5	0.27	-	32	273	2.3	

\* % water penetration is defined as the % of weight gain upon 24 hour water contact on the coated side without applied pressure. The notation "Wettable" means that the membrane became soaked with water by that time.



TABLE 8

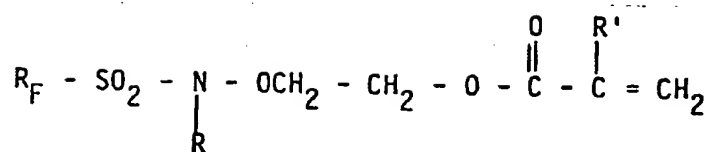
RESIN	M <sub>n</sub> <sup>(1)</sup>	Function-		R <sub>1</sub> <sup>(3)</sup>	R <sub>2</sub> <sup>(4)</sup>	R <sub>3</sub> <sup>(5)</sup>
		ality	%N <sup>(2)</sup>			
D	2000	2	3.78	HEA	IPDI	BD-ADA
F	1200-1400	2	4.35	HEA	IPDI	EG-ADA

## Footnotes for Table 4:

- (1) M<sub>n</sub> is the number average molecular weight based on the stoichiometry of the building blocks, R<sub>1</sub>, R<sub>2</sub> and R<sub>3</sub>.
- (2) %N based on elemental microanalysis.
- (3) HEA is 2-hydroxyethylacrylate
- (4) IPDI is 3-isocyanatomethyl-3,5,5-trimethylcyclohexylisocyanate, also known as isophorone diisocyanate.
- (5) EG-ADA is the repeat unit of the polyester polyol based on the condensation product of ethylene glycol and adipic acid. BD-ADA is the repeat unit of polyester polyol based on the condensation product of 1,4 butanediol and adipic acid.

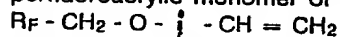
## Claims

1. A method for manufacturing microporous membranes (10) comprising the steps of:
  - A. mixing into a liquid vehicle a precursor material which is 1) rapidly polymerizable under ultraviolet or electron beam irradiation to a solid polymer, which is insoluble and nondispersible in the liquid vehicle such that when the polymers are formed it rapidly segregates from the liquid vehicle, and 2) selected from the group consisting of the organic monomers, the organic oligomers and mixtures thereof which are soluble in the liquid vehicle whereby upon said mixing there results a composition which is a liquid solution of said material in said liquid vehicle, said liquid vehicle being chemically inert relative to said material;
  - B. forming said composition into a thin liquid layer;
  - C. exposing the liquid layer to ultraviolet or electron beam irradiation to finally cure the liquid layer and,
  - D. removing the liquid vehicle from the membrane, characterised in that the precursor material includes a hydrophobic monomer or monomers and/or a support material is applied into intimate contact with the liquid layer before final curing thereof.
2. A method as set forth in claim 1 wherein said hydrophobic monomer is 1,1,3,3-tetramethylbutylacrylamide (t-octylacrylamide or TOCTAM).
3. A method as set forth in claim 1 or 2 wherein said hydrophobic monomer comprises between 8 to 33% by weight of the polymerizable material in the formulation.
4. A method as set forth in claim 1 wherein said hydrophobic monomer is an acrylic perfluoromonomer of the formula



where  $R_F$  is a perfluoroalkyl radical,  $C_kF_{2k+1}$ , where  $k$  is essentially 6 to 10,  $R$  is of the formula  $C_mH_{2m+1}$

where  $m = 2-4$ , and  $R'$  is hydrogen or methyl, providing hydrophobicity to the microporous film, or a perfluoroacrylic monomer of the structure



where  $R_F = C_z F_{2z+1}$ , and  $z = 6-8$ .

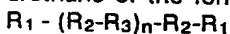
5. A method as set forth in claim 4 including said perfluoromonomer as 3% to 25% by weight of said polymerizable material in said solution.

6. A method as set forth in any preceeding claim wherein the support material (14) is applied into intimate contact with the liquid layer before final curing thereof and further including the step of exposing the thin liquid layer to electron beam or ultraviolet radiation to partially polymerize said precursor material, prior to applying the support material (14) into intimate contact with the original thin liquid layer.

7. A method as set forth in claim 6 wherein the further step is carried out in the presence of atmospheric oxygen.

8. A method as set forth in any preceeding claim wherein said step of forming said composition into a thin layer is further defined as spreading said composition on to a support surface (16) such as a moving belt.

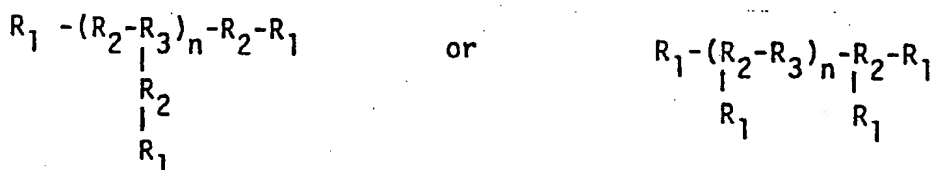
9. A method as set forth in any preceeding claim wherein said oligomeric material is an acrylic polyester urethane of the formula



where  $R_1$  is the radical of an hydroxy terminated acrylate monomer such as hydroxyethylacrylate, hydroxypropylacrylate and 4-hydroxybutyl acrylate;  $R_2$  is the dicarbamate or tricarbamate group resulting from the reaction of the isocyanate materials selected from the group consisting of di- and/or tri-aliphatic or aromatic isocyanates;  $R_3$  being selected from the group of polyester polyols made from the condensation of adipic acid with each one of or a mixture of ethylene glycol, diethyleneglycol, butanediol, hexanediol, and neopentylglycol,  $R_3$  having a number average molecular weight of 200 to 3000 and  $n$  equalling 0 to 4, or a mixture of such oligomers.

10. A method as set forth in claim 9 wherein the percent nitrogen associated with carbamate functionality of said oligomers is in the range of  $1.5 \pm 0.3\%$  to  $6.2 \pm 0.3\%$ .

11. A method as set forth in claim 9 wherein the formula is modified to



wherein the structure of the poly functional acrylates results from using trifunctional polyol and trifunctional isocyanates respectively.

12. A method as set forth in any preceeding claim further including the step of mixing a cross linking monomer with said precursor material in said liquid vehicle.

13. A method as set forth in claim 12 wherein said crosslinking monomer is a difunctional or trifunctional acrylate ester crosslinking monomer, or mixture thereof.

14. A method as set forth in claim 12 or 13 wherein said cross linking monomer comprises less than or equal to 50% (weight/weight) of the polymerizable material in the mixture.

15. A method as set forth in any preceeding claim further including the step of mixing one or a combination of monofunctional monomers with precursor material in said liquid vehicle.

16. A method as set forth in claim 15 wherein said monomer is from the group of monofunctional acrylate esters acrylamides, n-vinylpyrrolidone and n-vinyl lactam.

17. A method as set forth in claim 16 wherein said monomer comprises less than or equal to 50% (weight/weight) of the polymerizable material in the mixture.

18. A method as set forth in any preceeding claim wherein said liquid vehicle is from the group having the formula of  $CH_3 (CH_2)_n COOR'$

where R' equals methyl, ethyl, or isopropyl, and n equals 6-16 or having the formula of,  $R^*OCO(CH_2)_nCOOR^*$

where n equals 3 to 8 and R\* equals methyl, ethyl, isopropyl, butyl, isobutyl, octyl and isooctyl.

19. A method as set forth in claim 18 wherein said liquid vehicle further consists of butylcellosolve acetate in combination with said liquid vehicle.

20. A method as set forth in any preceding claim wherein the weight percent of said liquid vehicle in said mixture is from 40 to 80 percent.

21. A method as set forth in claim 20 further including the step of reducing the pore size of said membrane laminate by decreasing said weight percent of liquid vehicle.

22. A method as set forth in any preceding claim further including the step of adjusting the cloud point temperature of the mixture to alter the pore size of said membrane.

23. A method as set forth in any preceding claim further including the step of mixing surfactants with said oligomer in said liquid vehicle.

24. A method as set forth in any preceding claim wherein said support material (14) is a woven or nonwoven fabric.

25. A method as set forth in claim 24 wherein said nonwoven fabric consists essentially of nonwoven polyamide, polyester, cellulose derivative or corona discharge treated polypropylene.

26. A method as set forth in claim 8 wherein after applying the support material (14) said liquid layer is exposed to ultraviolet light which is passed through said support (14) to finally cure said liquid layer.

27. A method as set forth in claim 26 wherein said belt is made from a transparent release film made of silicone coated polypropylene or polyester, and said liquid layer is exposed to ultraviolet irradiation from below said moving belt.

28. A method as set forth in any preceding claim including the step of rolling said laminate (10) prior to removing said liquid vehicle.

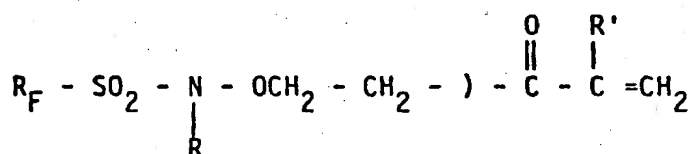
29. A method as set forth in any preceding claim including the step of forming a first and second laminate (10,10'), applying said mixture of liquid vehicle and precursor between the polymerized liquid vehicle layers (14,14') of the first and second laminates (10,10') and exposing said mixture to ultraviolet or electron beam irradiation to finally cure the liquid layer and to form a multilayer composite laminate.

30. A membrane comprising a microporous polymerized layer (12) of a precursor material which forms a homogenous solution with a liquid vehicle and 1) is rapidly polymerizable under ultraviolet or electron beam irradiation to said polymerized material (12), which is insoluble and nondispersable in the liquid vehicle, and 2) is selected from the group consisting of the organic monomers, the organic oligomers and mixtures thereof which are soluble in the liquid vehicle, the liquid vehicle being inert relative to said precursor material, characterized in that said precursor material includes a hydrophobic monomer or monomers and/or a support material (14) laminated directly to said microporous polymerized material (12).

31. A membrane as set forth in claim 30 wherein said hydrophobic monomer is 1,1,3,3-tetramethylbutylacrylamide (t-octylacrylamide or TOCTAM).

32. A membrane as set forth in claim 31 including TOCTAM and said hydrophobic monomer comprises between 8% to 30% by weight of said polymerizable material in said solution.

33. A membrane as set forth in claim 32 wherein said hydrophobic monomer is an acrylic perfluoromonomer of the formula



where  $R_F$  is a perfluoroalkyl radical,  $C_kF_{2k+1}$ , where k is essentially 6 to 10, R is of the formula  $C_mH_{2m+1}$

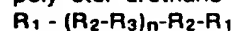
where m = 2-4, and R' is hydrogen or methyl, providing hydrophobicity to the microporous film, or a perfluoroacrylic monomer of the structure



where  $R_F = C_zF_{2z+1}$ , and z = 6-8.

34. A membrane as set forth in claim 33 including perfluoromonomer as 3% to 25% by weight of said polymerizable material in said solution.

35. A membrane as set forth in any of claims 30 to 34 wherein the oligomeric material is an acrylic polyester urethane of the formula

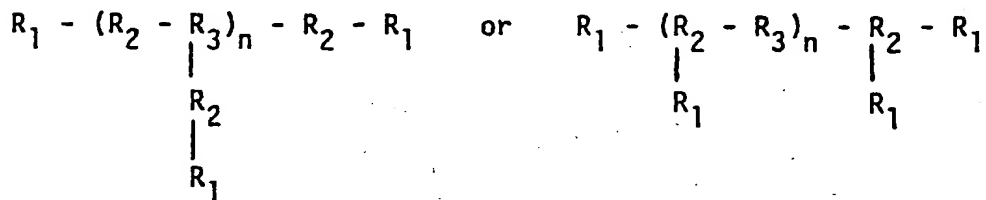


where  $R_1$  is the radical of an hydroxy terminated acrylate monomer such as hydroxyethylacrylate, hydroxypropylacrylate and 4-hydroxybutylacrylate;  $R_2$  is the dicarbamate or tricarbamate group resulting from the reaction of the isocyanate materials selected from the group consisting of di- and/or tri-aliphatic or aromatic isocyanates; and  $R_3$  is selected from the group of polyester polyols made from the

condensation of adipic acid with each one or a mixture of ethylene glycol, diethyleneglycol, butanediol, hexanediol, and neopentylglycol,  $R_3$  having a number average molecular weight of 200 to 3000 and  $n$  equalling 0 to 4.

36. A membrane as set forth in claim 35 wherein the weight percent nitrogen associated with carbamate functionality of said oligomers is in the range of  $1.5 \pm 0.3\%$  to  $6.2 \pm 0.3\%$ .

37. A membrane as set forth in claim 35 or 36 wherein the formula is modified to



wherein the structure of the poly functional acrylates results from using trifunctional polyol and trifunctional isocyanates respectively.

38. A membrane as set forth in any of claims 30 to 37 wherein said microporous material includes a crosslinking monomer.

39. A membrane as set forth in claim 38 wherein said crosslinking monomer is a difunctional or trifunctional acrylate ester crosslinking monomers or a mixture thereof.

40. A membrane as set forth in any of claim 30 to 39 wherein said microporous material includes a monofunctional monomer from the group of monofunctional acrylate esters, acrylamides, n-vinylpyrrolidone and n-vinyl lactam.

41. A membrane as set forth in claim 40 wherein said monomer comprises less than or equal to 50% (weight/weight) of the polymerizable material in the membrane.

42. A membrane as set forth in any of claims 30 to 41 wherein said support material (14) is a nonwoven fabric.

43. A membrane as set forth in claim 42 wherein said nonwoven fabric consists essentially of nonwoven polyamide, polyester, cellulosic derivative or corona discharge treated polypropylene.

44. A membrane as set forth in any of claims 30 to 42 wherein said laminate includes two inner layers (12,12') of said polymerized material and two outer layers (14,14') of said support material.

45. A membrane as set forth in any of claims 30 to 44 wherein said support material (14) has interstitial spaces, said polymerized material (12) being at least partially disposed within said spaces.

46. A membrane as set forth in any of claims 30 to 45 including a plurality of layers of said cured microporous material (12).

47. A membrane as set forth in claim 46 wherein each of said layers have different physical and chemical properties.

FIG. 1



Fig. 1

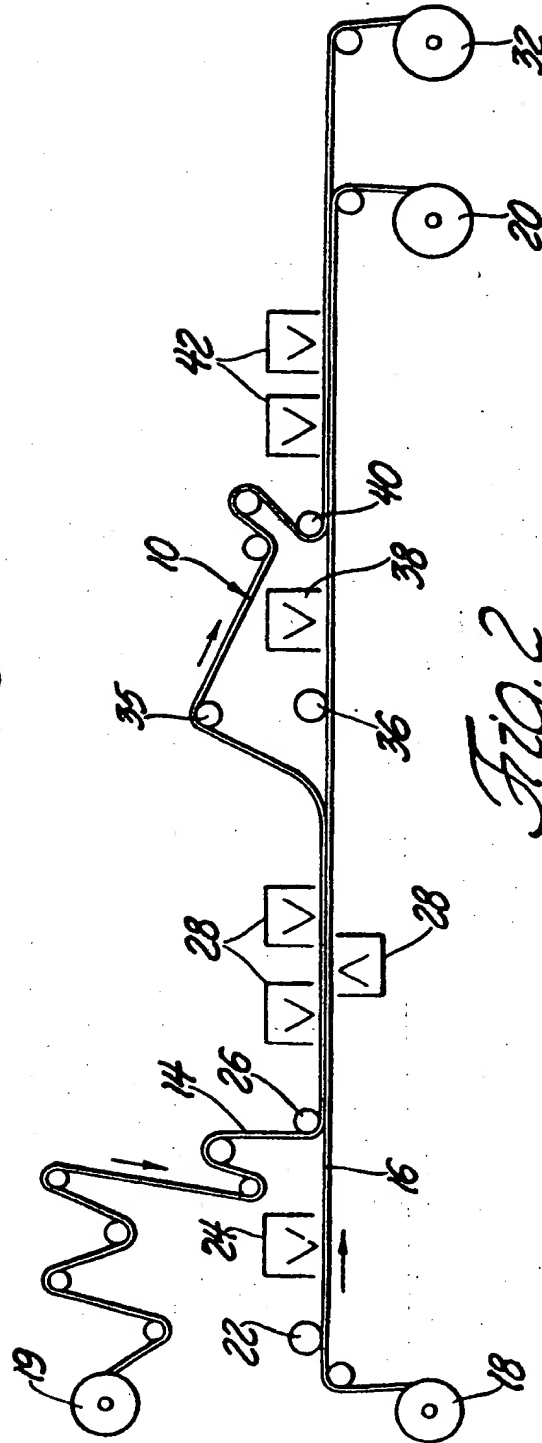
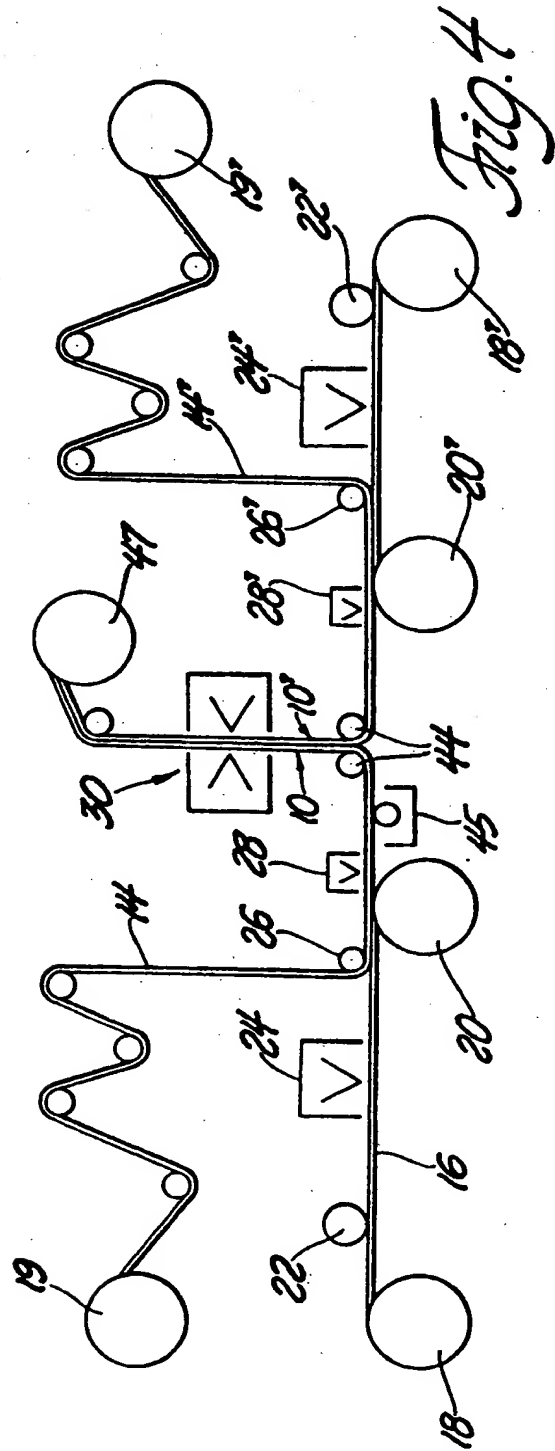
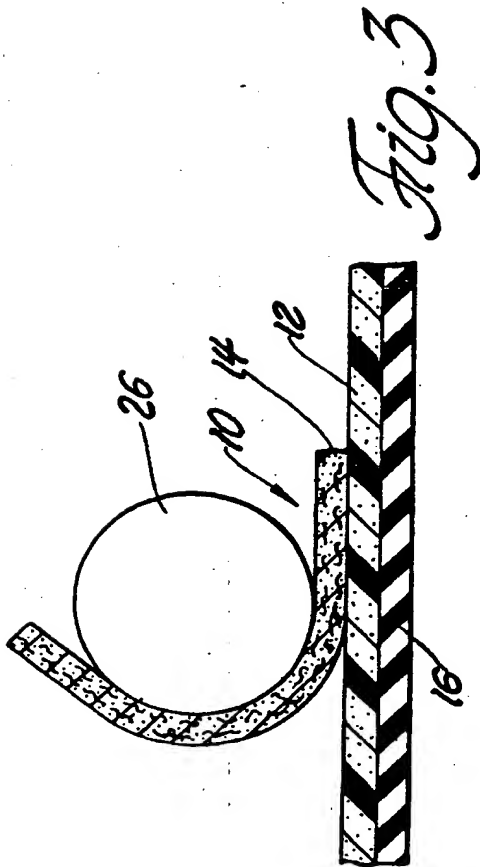
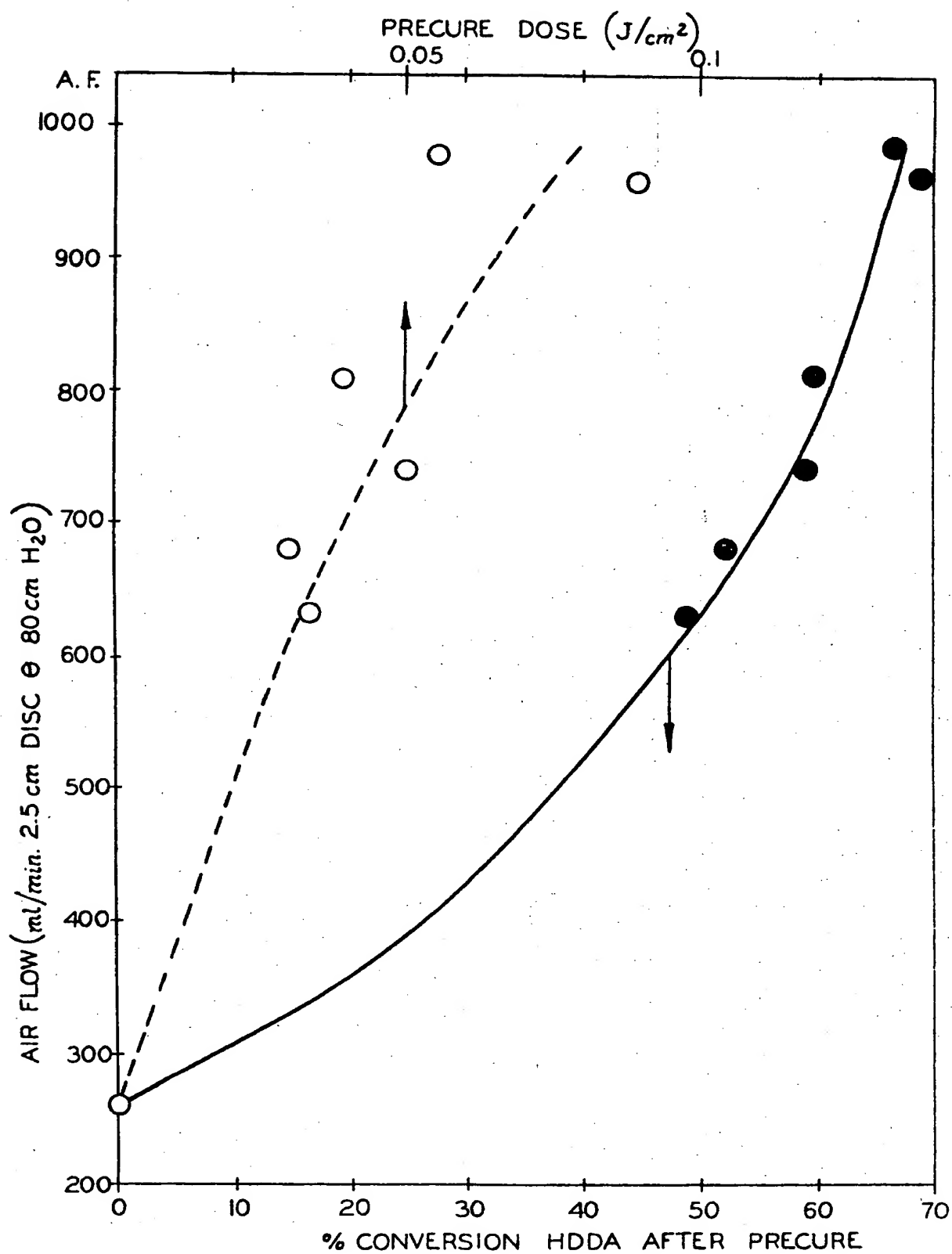


Fig. 2

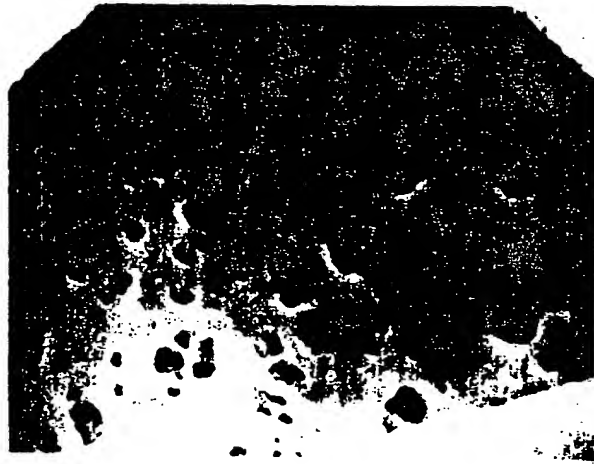
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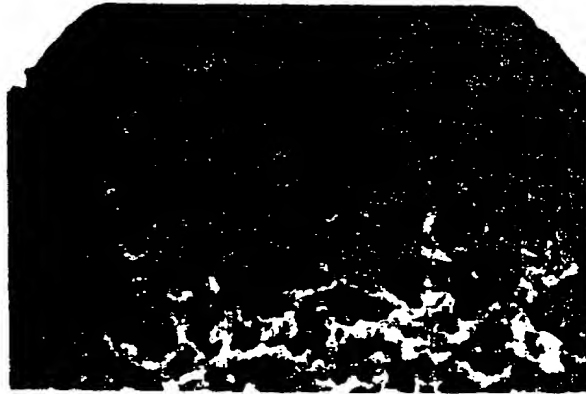


*Fig. 6*



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*Fig. 7**Fig. 8*



*Fig. 9*



*Fig. 10*



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Europäisches Patentamt  
European Patent Office  
Office européen des brevets

(11) Publication number:

**0 216 622**  
**A3**

(12)

# EUROPEAN PATENT APPLICATION

(21) Application number: 86307259.1

(51) Int. Cl. 4: **C08J 9/28**, **B01D 13/04**,  
**C08F 2/48**, **B32B 5/18**,  
**B32B 5/24**

(22) Date of filing: 22.09.86

(30) Priority: 23.09.85 US 778969  
23.09.85 US 778970

(43) Date of publication of application:  
01.04.87 Bulletin 87/14

(84) Designated Contracting States:  
**AT BE CH DE FR GB IT LI LU NL SE**

(88) Date of deferred publication of the search report:  
27.07.88 Bulletin 88/30

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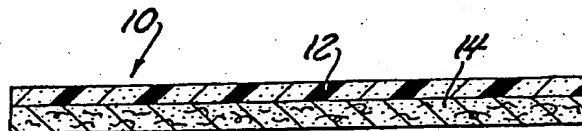
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## (54) Microporous membrane laminate.

(57) A membrane or laminate (10) consisting essentially of microporous polymerized material (12) consisting essentially of a precursor material which forms a homogenous solution with a liquid vehicle and is 1) rapidly polymerizable under ultraviolet or electron beam irradiation to a polymerized material, which is insoluble and nondispersible in the liquid vehicle, and 2) selected from the group consisting of organic monomers, organic oligomers, and mixtures thereof which are soluble in the liquid vehicle, the liquid vehicle being inert relative to the precursor material and optionally a support material (14) laminated directly to the microporous material. The precursor microporous material may include a hydrophobic monomer. The instant invention further provides a method for manufacturing the fluid permeable microporous membrane laminate (10) including the steps of mixing the precursor material into the liquid vehicle, forming the composition into a thin liquid layer, applying a support material (14) into

intimate contact with the liquid layer, exposing the combined liquid layer and support material (14) to ultraviolet or electron beam irradiation to finally cure the liquid layer and form a laminate with the support material 14, and removing the liquid vehicle from the laminate (10).



*Fig. 1*

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DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.4)
A	<u>GB - A - 2 025 425</u> (AMERACE CORPORATION) * Claims 1,2,11,24,29,42-44, 48 *	1,12, 13,24, 25,30, 38,42, 43	C 08 J 9/28 B 01 D 13/04 C 08 F 2/48 B 32 B 5/18 B 32 B 5/24
D,A	<u>US - A - 4 466 931</u> (TANNY) * Claims *	1,8, 20	
A	<u>US - A - 4 404 073</u> (BARTISSOL et al.) -----		
			TECHNICAL FIELDS SEARCHED (Int. Cl.4)
			C 08 J B 01 D C 08 F 2/00 B 32 B 5/00
The present search report has been drawn up for all claims			
Place of search VIENNA		Date of completion of the search 09-05-1988	Examiner WEIGERSTORFER
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